

**FLAMMABILITY AND TOXICOLOGICAL CHARACTERISTICS
OF ISOCYANURATE FOAMS,
INTUMESCENT COATINGS AND FLUOREL**



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F I N A L R E P O R T

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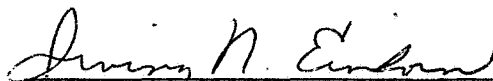
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Research was conducted according to the principles enunciated in the "Guide for Laboratory Animal Facilities and Care," prepared by the National Academy of Sciences-National Research Council

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ABSTRACT

An experimental program was conducted to study the thermochemical, flammability, and toxicological characteristics of JP-4 aircraft fuel, isocyanurate foams, intumescent coatings, and Fluorel. Testing methods included XP-2 chamber smoke test, ASTM D-1692, infrared photography, Bureau of Mines penetration test, and use of the Instron Environmental Chamber to measure compressive strength. Combustion and pyrolysis gases were analyzed by gas chromatography and mass spectrometry. The LD-50 test was performed on Sprague-Dawley rats housed in an environmental chamber. The isocyanurate foam, fluorel-coated foam, and the intumescent-coated foam were found to have excellent flammability and insulation characteristics, although smoke development was substantial. The LD-50 values for Sprague-Dawley rats, based on a two-week survival, were approximately 2.0 gm/ft^3 for all three materials.

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I. INTRODUCTION

A. BACKGROUND

Previous studies of low-density foams have indicated their utility, if properly designed and formulated, as an effective char precursor. Exposure of fire-retardant isocyanurate foams in large scale JP-4/air fuel fires have demonstrated their excellent resistance to flame penetration and their effectiveness as a thermal barrier. The application of an intumescent barrier coating to the isocyanurate foam improves the flammability characteristics of the cellular substrate, retards the outward diffusion of gaseous degradation products, and leads to the earlier formation of a stable char structure.

The application of a fluorinated polymeric coating, a copolymer of vinylidene fluoride and hexafluoropropylene to polymeric materials, has been selected by NASA/Houston as a second method for providing additional stability to substrates during actual fire exposure.

Both of the above described systems offer marked improvement of the flammability characteristics of materials in actual fire exposure. However, considerable concern has been raised as to possible undesirable side effects to life support during pyrolysis or combustion.

B. PREVIOUS STUDIES

In a continuing program sponsored by the Chemical Research Section NASA/Ames, the Center For Flammability Research of the University of Utah previously evaluated the thermochemical and thermophysical properties of low-density fire-retardant urethane foams. These results are presented

in Reference 10.

II. SCOPE OF WORK

As outlined in Contract NAS2-6063, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California, the specific objectives of this work were:

- A. To determine the initial physiological response to burning JP-4 fuel, to serve as a baseline for comparing the toxicity of combustion products from isocyanurate foams, fluorel refset and 45-B-3 coatings. This was to be accomplished by determining the effect of temperature and oxygen concentration on laboratory rats.
- B. To determine the flammability characteristics and pyrolysis products of coated and uncoated foams. In addition, gross analysis of the effects of effluents from these materials was to be made by determining the LD-50 lethal dose of pyrolysis products.
- C. To determine the degree of light obscuration of burning Ames Intumescent Coating, 45-B-3, and the LD-50 lethal dose of pyrolysis products from this intumescent coating.
- D. To identify the effluent gases resulting from pyrolysis of Fluorel Refset and to determine LD-50 lethal dose of these products.

The studies reported herein were designed to meet the objectives of the contract. In addition to the studies specified above, determination of the cause of death was made on a limited number of Sprague-Dawley rats. Necropsies were performed on selected animals which were killed in fire

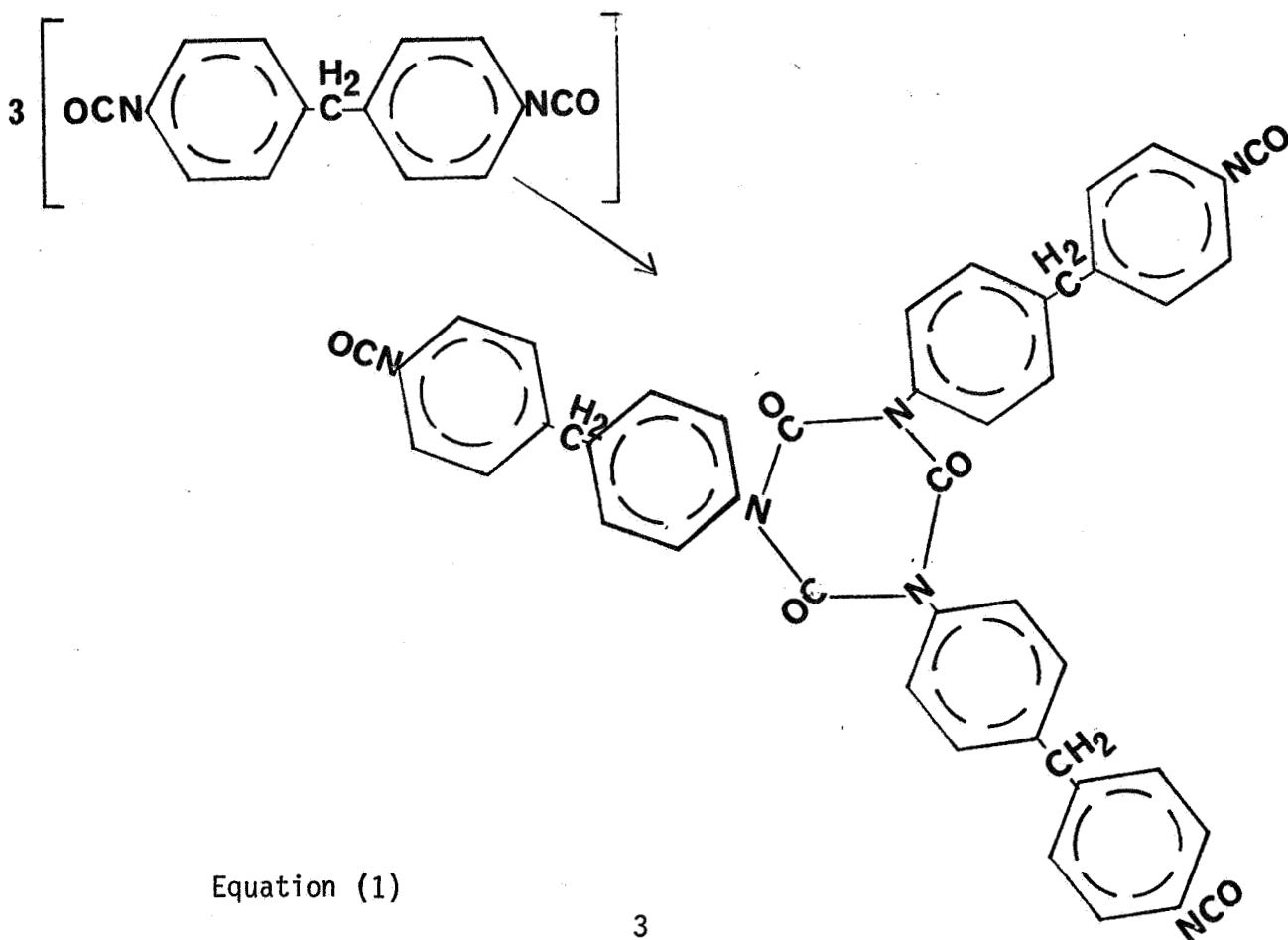
exposure tests and, in addition, histopathological studies of the respiratory tract and vital organs were conducted to determine the nature and extent of injury.

The results of these studies and their significance has been considered and used to design further experiments in an attempt to ascertain the relevance between animal studies and human response.

III. DESCRIPTION OF MATERIALS

A. CHEMISTRY OF ISOCYANURATE POLYMERS

The isocyanurate ring structure is formed by the cyclization of three isocyanate groups. Increased thermal stability and improved flammability characteristics may be obtained by the incorporation of polyfunctional aromatic isocyanates such as 4,4' diphenylmethanediisocyanate. The cyclization reaction is shown in Equation (1).



Equation (1)

Farkas and Mills⁽¹⁾ reported using base catalysts such as sodium benzoate, lead oleate, and tertiary amines to control the cyclization process. The highly aromatic structure of the isocyanurate polymers restricts motion in the polymer chain and produces brittleness.

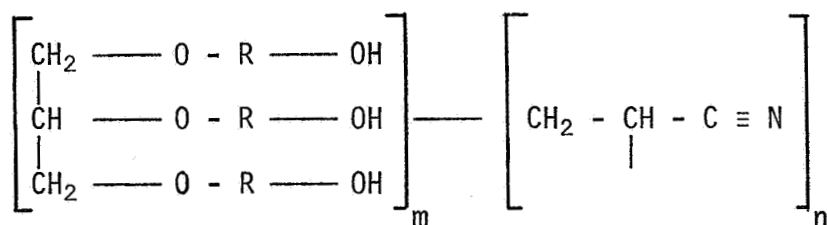
Riccitiello, et.al.⁽²⁾ introduced urethane linkages into the isocyanurate polymer to obtain the desired degree of flexibility. The major disadvantage to modification of the polymer by the addition of urethane linkages is the reduction in thermal stability of the modified polymer. Urethane linkages decompose at lower temperatures than the isocyanurate structure. Depending on the nature of the isocyanate structure, polyol functionality, and molecular-weight-per-crosslink density the urethane linkages decompose from 180°C to 275°C with a char yield ranging from 0 to 35 percent.⁽³⁾ The isocyanurate ring structure decomposes between 300°C and 325°C with an approximate char yield of 50 percent. Isocyanurate polymers modified by the introduction of urethane linkages while possessing a reduced thermal stability have reduced brittleness and friability, increased dimensional stability, and produce a higher char yield than comparable rigid urethane foams.

The polyol moiety can greatly influence the flammability characteristics of the cellular plastic. Riccitiello, et.al.⁽²⁾ listed four parameters which govern the development of char yield, the flammability of decomposition species, and the thermal degradation temperature of isocyanurate polymers:

1. The polyol moiety must serve as a precursor to char formation which may form as result of a cyclization process.
2. The temperature for cyclization should occur prior to that required for the degradation of the urethane linkage to minimize volatile fragment formation.
3. The polyol should have a low hydroxyl number to limit the conversion of isocyanurate groups to urethane linkages.

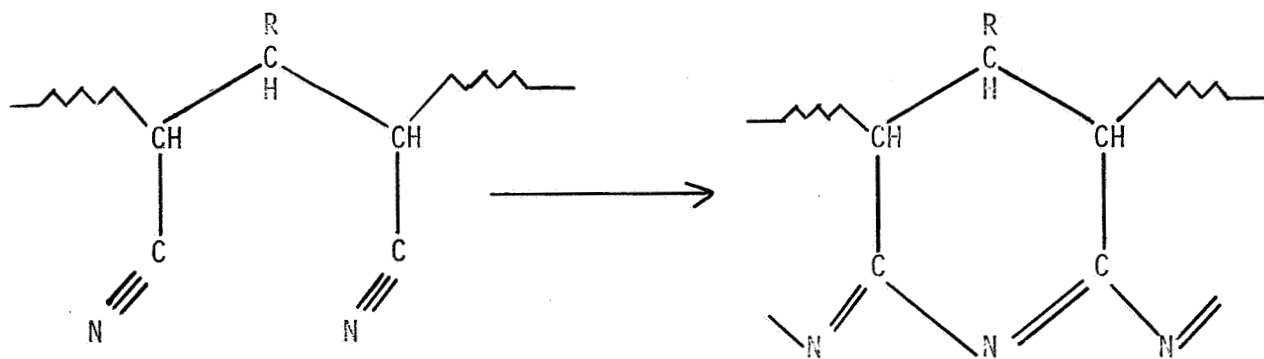
4. The polyol should have a high molecular weight and low functionality in order to impart mechanical flexibility to the isocyanurate-urethane polymer structure.

The polyol used to prepare the isocyanurate polymers developed by NASA/Ames was a prepolymer derived from glycerin and propylene oxide to which pendant nitrile functional groups were grafted. The polyol has the following structure:



STRUCTURE OF POLYOL

Acrylonitrile was selected as the grafting monomer because nitrile linkages cyclize to form a high-temperature-stable heterocyclic structure at temperatures below 200°C. The cyclization reaction of the nitrile group is:



CYCLIZATION OF NITRILE GROUPS

The homogeneous char structure which is formed in high yield acts as an effective diffusion barrier and thus retards the migration of volatile degradation products into the gaseous phase. This carbonaceous layer also provides an effective thermal insulation barrier to shield the underlying substrate from the burning region.

The reaction of isocyanate and polyol produced an exotherm sufficiently high to volatilize the trichlorofluoromethane blowing agent incorporated in the polyol thus producing a rigid cellular plastic. The foamed isocyanurate polymer had a nominal density of 2.5 - 2.7 lbs./ft.³ This closed celled foam (92% closed-cell content) had an initial thermal conductivity of 0.150 BTU.in./ft.²hr.⁰F. The physical properties of the Ames isocyanurate foam are presented in Table I.⁽²⁾

TABLE I
PROPERTIES OF AMES ISOCYANURATE FOAM

<u>Physical Property</u>	<u>Observed Values</u>	<u>ASTM Test Method</u>
Nominal Density	2.5 - 2.7 lbs./ft. ²	D-1622
Thermal Conductivity	0.150 BTU.in./ft. ² hr. ⁰ F.	C-177
Flame Resistance	Self-extinguishing	D-1692
Compressive Strength ()	27 p.s.i.	D-1621
Compressive Strength (⊥)	19 p.s.i.	D-1621
Compressive Modulus ()	1000 p.s.i.	D-1621
Compressive Modulus (⊥)	500 p.s.i.	D-1621
Water Absorption, Volume %	3.5%	D-2127

IV. PYROLYSIS PRODUCTS OF JP-4 AIRCRAFT FUEL

A. ANIMALS AND ANIMAL CARE

White male Sprague-Dawley rats were procured from the Holtzman Company through the Vivarium of the University of Utah. Upon delivery to the Vivarium, the animals were placed in isolation and maintained on a diet modified with antibiotics for a period of ten days before use in laboratory experiments. Randomly selected rats were sacrificed for pathological and histological studies, both to ascertain their normal condition prior to their use in experimentation and to obtain data on animals which would be used as control specimens.

B. DESCRIPTION OF CHAMBERS AND ANALYTICAL EQUIPMENT

1. Laboratory Animals Environmental Test Chamber

Several concepts involving a completely designed chamber were initially considered. However, it was found possible to shorten construction time and still maintain the cost of the unit to within an acceptable amount by basing the final design on a modification of a commercial forced-draft oven. The particular oven selected was a Blue M Stabil-Thermtm oven, which has a stainless-steel interior and excellent temperature control between 100⁰ and 500⁰F. The oven was modified to permit

exposure of up to 16 animals with no loss or significant dilution of the test atmosphere. This was accomplished by the addition of an air-lock and a sliding-animal-chamber holder. The modified environmental test chamber is shown in Figure 1. Locations of monitoring and sample ports are indicated in the sketch. Initial experiments were designed to determine the onset of physiological change, the LD-50 level, and the LD-100 level of response. Provisions were made to telemeter blood circulatory rates, respiratory rate, brain wave pattern, and animal body temperature during exposure by recorders as indicated. An interior view of the animal chamber shown in Figure 2 indicates the sliding chambers and air-lock feature incorporated to permit introduction of the animals into the chamber without disturbing the environment. Special O-rings were required to provide a gas-tight seal. A glass window was installed together with interior lighting to permit observation and photography of animal response. An individual animal chamber is shown in Figure 3 utilizing a borosilicate-glass tubular enclosure and stainless-steel mesh-screen end enclosures. In later experiments, chambers were constructed entirely of stainless-steel mesh to permit better flow-through of circulating gases. Multiple chambers were held together using the assembly device shown in Figure 4.

2. Non-Corrosive Environmental Chamber

Early experiments indicated that problems might be encountered with surface adsorption of degradation gases on metal walls and with

corrosion. Therefore, a second chamber, as shown in Figure 5, was fabricated of polymethylmethacrylate to permit direct pyrolysis and other corrosive-gas studies. Experience indicated little or no attack on the plastic components of the chamber.

C. GROSS EFFECT OF TEMPERATURE ON LIFE

1. Animal Exposure to Elevated Temperatures

To determine the effects of temperature on survival time, 46 Sprague-Dawley male rats, weighing from 40 to 265 g were exposed to temperatures ranging from 50°C to 240°C. Observations of the animals' behavior were noted and the time to death recorded. Death was determined by visual observation of the cessation of breathing.

The behavior of animals was quite similar at all temperatures with animals being concerned about their paws and ears within 30 to 45 seconds after introduction into the chamber. Sporadic, but not panicky movement, was noted at all temperatures, interspersed with short periods of quiet behavior during which the animals appeared to moisten their paws and rub their ears. Death was usually preceded by convulsions which at first were generally restricted to the head and front quarter of the animal. Following the mild convulsions the eyes would close and irregular (usually shallow) breathing would occur followed by severe muscular spasms throughout the entire body. Death would occur shortly after the onset of the whole body convulsions. These characteristic responses were noted at all temperatures with longer time lapses between symptoms at lower temperatures for all weight classes. Less than 3 percent weight loss was found for animals at all temperatures indicating that severe

body dehydration had not occurred.

When the data were plotted as temperatures versus time of death (LD-100) three distinct curves were obtained which were nearly parallel. These curves were found to be a function of the animal's weight with the largest animals surviving the longest, (see Figure 6). All animals died between three and four minutes at 230°C . There appeared to be an induction period during which the chamber came back to a steady-state condition. The longest observed survival time was 44 minutes for a 100 g rat at 52°C . When the data are plotted as temperature versus log of survival time (Figure 7) two straight lines were found to intersect at about 100°C for the 100 gram animals. The slope of the curve for temperatures greater than 100°C is about $22^{\circ}\text{C}/\text{minute}$, while the slope of the second line is about $0.5^{\circ}\text{C}/\text{minute}$. The distinct changes in slope probably indicate two different mechanisms causing death. However, further investigations are required to substantiate this premise.

A third plot of the data is shown in Figure 8 where exposure time (minutes) multiplied by temperature ($^{\circ}\text{C}$) and divided by body weight is plotted as a function of temperature ($^{\circ}\text{C}$). Though the full meaning of the plot is not understood at this time, three distinct nearly parallel curves were found according to body weight, which intersected with a single common line for temperatures below 80°C . While further study is required these curves strongly indicate the animals are overwhelmed by heat and their system cannot respond quickly enough to permit them to accommodate to the sudden increase in temperature.

The strongest implications of these experiments is that death due to heat alone is significant at elevated temperatures and that future testing with gases and temperature should meaningfully be restricted to

temperatures below 80°C. However, tests should be run to measure the short-term exposure hazards of animals in fires simulating aircraft-crash fires, home fires, etc.

Additional experiments must be conducted to assess the effect on body systems and organs when animals are subjected to sublethal exposures during fires.

2. Comparison of Animal and Human Survivability

The thermal tolerance of the Sprague-Dawley rats is compared to that of humans in Figure 9 as a function of time of exposure. The curve for humans is based on the data of Pryor⁽⁴⁾ (Southwest Research Institute). At very high temperatures, the small rats appear to have a much greater thermal tolerance than humans. This may be due to the insulating fur of the rats. At the lower temperatures, however, humans can tolerate such levels for longer periods of time. This may be due to a more favorable surface-to-volume ratio for humans.

Despite the apparent importance of the insulating fur, a preliminary treatment of the ambient temperature--time data for the rats in terms of a lumped parameter transient heat conduction problem was attempted assuming a process controlled by external combined effective heat transfer coefficient for convection and radiation. The governing equation is:

$$\ln \left(\frac{T_a - T_b}{T_a - T} \right) = \frac{h}{\rho C_p} \left(\frac{A}{V} \right) \theta$$

Equation (3)

Where: θ = Time

T_a = Ambient temperature

T_b = Initial animal temperature

T = Minimum animal temperature that can cause death

h = External combined heat transfer coefficient

$\frac{A}{V}$ = Animal surface-to-volume ratio

ρ = Animal density

C_p = Animal specific heat

If Equation (3) is valid, a plot of $\log \left(\frac{T_a - T_b}{T_a - T} \right)$ versus θ should yield a straight line. It was found that if the data for the small rats were processed using a value of $T = 45^\circ \text{C}$ (minimum human body temperature that can cause death is approximately 42°C), a reasonable straight line was obtained. From the slope of the line, a value for h of $4.0 \text{ BTU/hr.} \cdot \text{ft.}^2 \cdot ^\circ \text{F.}$ was approximated. This is not unreasonable. Further treatment of the thermal tolerance experimental data as a heat transfer problem is planned in future studies.

D. GROSS EFFECTS OF OXYGEN CONCENTRATION ON LIFE

1. Oxygen-Temperature Interaction

Data on the effect of oxygen concentration on rat survival are available from the work of Pryor, et.al.⁽⁴⁾ Pertinent information to our study are shown in Table II. These data indicate that at least a 9% oxygen concentration is necessary to insure life at 85°F.

E. COMBUSTION PRODUCTS - JP-4 JET FUEL

Considerable difficulty was encountered in measuring gas composition during combustion experiments involving JP-4 fuel. Method of burning and position of sampling were major variables. Some of these data are summarized in Table III for combustion products of JP-4 fuel obtained by sampling at two places in a flame. When sampled in a closed container or when attempts were made to collect combustion products

TABLE II
ANIMAL EXPOSURE TO PRIMARY VARIABLES

Oxygen Concentration	Temperature °F	Time of Exposure Hours	Survivors Out of 10
(Normal Concentration)			
21	100	24	10
21	110	24	10
21	115	24	10
21	120	24	7
21	120	4	7
16	85	24	10
11	85	24	10
9	85	24	10
7.5	85	24	6
7.5	85	4	7

above the flame the sample was too dilute (with air) to obtain reliable data. Sampling of the atmosphere was extremely difficult, in this respect, when animals were exposed to the combustion of JP-4 fuel.

The data in Table III represent the gaseous products (at room temperature) obtained by burning JP-4 on a quartz-wool wick and sampling the flame as indicated. The gases were separated with a 20-inch silica-gel column (100°C) in series with a 20-foot mole-sieve (90 percent 13x + 10 percent 5A) column using a thermal conductivity detector. While the same gaseous products were found throughout the flame, the quantities of the gases varied considerably according to the position, method of sampling, and the method of burning. Analysis of the small amounts of condensed liquids was not attempted.

A sample of JP-4 fuel combustion gas products was also analyzed in an initial control run in conjunction with testing of foams and coated foams with the fire simulation chamber as discussed below. The analysis was made with a gas chromatograph. The sample was withdrawn from the vent stack. On a water-free basis, the gas composition was 80.4% N_2 , 10.8% O_2 , and 8.8% CO_2 . This indicated that excellent combustion conditions could be achieved in the fire simulation chamber.

Theoretical calculations were also made of the equilibrium combustion products with various amounts of air and oxygen. These equilibrium calculations were carried out using a chemical equilibrium computer program. The results of the calculations are tabulated in the following tables. Table IV-A presents the equilibrium product mixtures that would occur in the case of normal octane in air after the gases had cooled to 1200°K . Octane was used to simulate JP-4. Table IV-B presents the results of equilibrium calculations for normal octane burned in air at 1.0

TABLE III
GASEOUS COMBUSTION PRODUCTS OF JP-4 JET FUEL (H₂O-Free Basis)

Sample Location	Top of Flame	Bottom of Flame
Mole Fraction Of Products:		
N ₂	0.821	0.775
CO ₂	0.074	0.093
CO	0.032	0.034
H ₂	0.014	0.029
O ₂	0.050	0.051
CH ₄	0.0072	0.0144
C ₄ H ₁₀	0.0015	0.0019

TABLE IV-A

EQUILIBRIUM BURNED-GAS COMPOSITIONS AT 1.0 ATMOSPHERE
PRESSURE AND 1200°K FOR OCTANE IN AIR

Per Cent Excess Fuel	0	20	30	50
Mole Fraction Of Products:				
N ₂	0.736	0.699	0.682	0.650
H ₂ O	0.140	0.125	0.117	0.101
CO ₂	0.124	0.103	0.0935	0.0773
CO	0.00000227	0.0391	0.0564	0.0875
H ₂	0.00000188	0.0348	0.0517	0.0842
NH ₃	0.000001	0.00000104	0.00000186	0.00000378

Products considered but present in concentration less than 1 ppm are
same as listed in Table IV-B.

TABLE IV-B

EQUILIBRIUM FLAME TEMPERATURES AND BURNED-GAS COMPOSITIONS AT
1.0 ATMOSPHERE PRESSURE FOR OCTANE IN AIR

Per Cent Excess Fuel	0	25	50	100
Flame Temp. °K	2273	2174	1984	1639
Mole Fraction Of Products:				
N ₂	0.727	0.689	0.649	0.581
H ₂ O	0.134	0.140	0.126	0.0806
CO ₂	0.110	0.0783	0.0529	0.0303
CO	0.0136	0.0678	0.112	0.167
H ₂	0.00304	0.0237	0.0597	0.141
NH ₃	10 ⁻⁶	10 ⁻⁶	10 ⁻⁶	10 ⁻⁶
O ₂	0.00615	0.000033	10 ⁻⁶	10 ⁻⁶
HO	0.00328	0.000612	0.0000747	10 ⁻⁶
NO	0.00257	0.000148	0.00000825	10 ⁻⁶
H	0.000462	0.000746	0.000353	0.000306
O	0.000331	0.0000131	10 ⁻⁶	10 ⁻⁶

Products considered but present in less than 1 PPM (10⁻⁶ mol fraction):

C ₈ (solid carbon)	CH ₄	C ₂ N ₂
C ₁ through C ₅ (carbon vapor)	O ₃	HCN
HCO	C ₃ O ₂	NH
HCHO	N	NH ₂
C ₂ H ₄ O	N ₂ O	higher hydrocarbons
CH	NO ₂	organic acids
CH ₂	N ₂ O ₃	higher carbonyls
CH ₃	N ₂ O ₄	peroxides
C ₂ H ₂	N ₂ O ₅	alcohols
C ₂ H ₄	CN	

atmosphere pressure at the flame temperature. A similar tabulation for normal octane in pure oxygen is given in Table IV-C.

It should be noted from the data in Table IV-B and Table IV-C that octane burned in air with no excess fuel yields a CO concentration an order of magnitude lower than if the same fuel is burned in pure oxygen. The CO concentration in octane-air equilibrium combustion was lower than if pure oxygen was the oxidizer and if the fuel was in excess.

In a real fire situation, the degree of local excess fuel depends on the level of turbulence, method of ignition and amount of ventilation. Consequently, it is difficult to accurately predict the expected distribution of combustion products without first knowing the conditions of the combustion in the actual fire situation.

Possibly, local excesses of fuel can result in concentrations of CO greater than the lethal dose.

F. ANIMAL EXPOSURE

Because of experimental difficulties, it was not possible to establish the desired toxicity baseline from the exposure of rats to the JP-4 combustion products. Typical data of animal exposures are given in Table V. Continued burning of the jet fuel to consume the desired amounts of fuel caused either excessive temperature rise or, more importantly, volatilized too much of the test specimen. Attempts to re-ignite the volatilized fuel resulted in explosion and flash fires which killed the test animals. Use of glass-wool wicks, electrical ignition alcohol fuel-type lamps, and direct ignition proved unsatisfactory. External burning, as with an atomizing nozzle, offers a potential solution to this problem.

TABLE IV-C

EQUILIBRIUM FLAME TEMPERATURES AND BURNED-GAS COMPOSITIONS AT
1.0 ATMOSPHERE PRESSURE FOR OCTANE IN OXYGEN

Per Cent Excess Fuel	0	25	50	200
Flame Temp. °K	3107	3114	3071	2785
Mole Fraction Of Products:				
O	0.510	0.336	0.162	0.000752
H ₂ O	0.280	0.286	0.278	0.205
CO	0.219	0.282	0.337	0.415
CO ₂	0.146	0.119	0.0907	0.0432
O ₂	0.101	0.0421	0.0129	0.000219
HO	0.0952	0.0784	0.0526	0.0849
H ₂	0.0567	0.0919	0.140	0.286
H	0.0514	0.0669	0.0729	0.0413
CH ₂ O	0.00000608	0.0000101	0.0000141	0.0000169

TABLE V
EFFECT OF JP-4 COMBUSTION PRODUCTS ON SPRAGUE-DAWLEY RATS

<u>JP-4 Sample Volume</u>	<u>Weight of Rats (gm)</u>				
	<u>Initial</u>	<u>1 Day</u>	<u>2 Days</u>	<u>3 Days</u>	<u>14 Days</u>
1 ml	385	390	404	412	435
2 ml	345	344	367	360	408
4 ml	365 (DOR)				
	Death 9-Minutes				

V. ISOCYANURATE FOAMS

A. SMOKE DEVELOPMENT

One of the many aspects that are of major concern when studying the flammability characteristics of materials is the analysis of the parameters governing the smoking tendency. As additives are incorporated into a polymer to retard its flammability, it is usually found that the quantity of smoke increases as flame propagation decreases. Most often the smoke emitted contains large amounts of carbon in the form of soot which readily obscures light.

In studies of the tendency of various fuels to smoke, Minchin⁽⁵⁾ and Clarke⁽⁶⁾ found that the tendency of paraffins to smoke increased with the molecular weight. On the other hand, for olefins, aromatic polymers, and compounds in the naphthalene series, the tendency to smoke was found to decrease with molecular weight. Figure 10 summarizes the tendency of fuels to smoke. Mickelson and Einhorn⁽⁷⁾ reported on studies carried out to determine the effect of reactive and non-reactive flame retardants on the smoke development in urethane polymers. This study also showed the effects of polymer structure on the development of char yield and light obscuration.

The smoke-development properties of isocyanurate foams and foam systems were studied using a modified XP-2 smoke-density chamber⁽⁸⁾ illustrated in Figure 11. The chamber measures 12 inches by 12 inches by 31 inches high and is constructed of anodized aluminum with stainless steel fittings. The door is cast aluminum with an inset fire-resistant plate glass panel to permit observation of the test specimens during burning.

A quantitative analysis of the smoke density is made by the use of a Weston Barrier Layer photocell incorporated in the walls of the

chamber 11 inches above the sample support. Normally, the time necessary to reach 100% light obscuration is used as a measure of the amount of smoke being produced. However, since the approach to 100% light obscuration is asymptotic, it is very difficult to obtain times to 100% obscuration which are reproducible. Moreover, some samples can be burned completely without ever producing enough smoke to give 100% light obscuration. For these reasons, the time necessary to reach 70% light obscuration was taken as the arbitrary criterion for comparing the smoke developed in the burning of various foam samples. For samples of the same material, the time to 70% light obscuration can be measured within a standard deviation of 0.4 seconds.

Two by two by two inch samples of isocyanurate foam (NASA samples 1a, 2a, 4a, 6a, and 8a) were evaluated using the XP-2 Smoke-Density Chamber. The samples were supported on a 1/4-inch stainless-steel grid and subjected to the direct impingement of a propane flame (1950°F - 50 psig gas pressure).

Figure 12 shows the smoke obscuration values obtained for the five uncoated isocyanurate foam samples under static conditions. The scatter in the data (maximum light obscuration values 62 - 71%) is attributed to the non-homogeneous cell structure of the specimens.

Figure 13 compares the average light obscuration values of the uncoated isocyanurate foams with those obtained for samples coated with the NASA intumescent coating and Fluorel coating under static conditions. The Fluorel-coated samples exhibited the least smoke development while the intumescent-coated samples produced the greatest volume of smoke after an initial lower induction period.

Figure 14 illustrates the smoke development characteristics observed when samples of the uncoated isocyanurate foam and coated foam systems were burned in the XP-2 Smoke Density Chamber with air flowing at 10cfm. These results show a trend opposite to those data obtained under static conditions (Figure 13). It is thought that insufficient air was present to permit continued combustion of the Fluorel and Intumescent-coated specimens under static conditions. The dynamic air environment provides a continual source of oxygen and thus the previously reported trend is reversed.

B. THERMAL ANALYSIS

Thermogravimetric analysis and differential thermal analysis of the unmodified isocyanurate foam resulting from the cyclization of a polymeric isocyanate and the modified polyol were carried out using a Dupont Model 950 Thermogravimetric Analyzer and a Dupont Model 900 Differential Thermal Analyzer.

The thermogravimetric analyses were conducted using a dynamic heating rate of 10°C per minute in flowing (100 cc/minute) air and nitrogen environments (Figure 15).

The initial weight loss (40-100°C) was attributed to evolution of polyol fragments. The weight loss occurring between 100°C and 200°C was identified as the C Cl₃F blowing agent. The weight loss from 200°C to 315°C was attributed to evolution of the tertiary amine catalyst.

Figure 16, the differential thermal analysis of the isocyanurate foams showed that a strong exothermic reaction commenced at 220°C in the air environment while an endothermic reaction was observed in the range of 282-294°C in the inert nitrogen environment.

C. PYROLYSIS STUDIES

A series of pyrolysis experiments, ranging in temperature from 200 to 1000°C, was made on isocyanurate sample 8-A using a Hewlett Packard 7626A Gas Chromatograph and pyrolysis attachment. Both the thermal conductivity detector (TCD) and flame ionization detector (FID) were used. A 10:1 effluent split ratio was used which allowed some distinction to be made between the light gases (non-oxidizable) and the other pyrolysis products which were oxidizable. The FID detects only oxidizable fractions, while the TCD senses all components. Separations were achieved on a 6' x 1.8" methylvinyl gum rubber column using helium gas flowing at a rate of 30 cc/min. Below 500°C only trace amounts of a few oxidizable materials plus the light gases were observed. Above 500°C more than 30 oxidizable fractions and a greatly increased quantity of non-oxidizable gases were detected. Positive identification of all the many separated peaks was not possible within the scope of this study. However, tentative identification of the halogenated blowing agent, the tertiary amine catalyst, water, and some fifteen other compounds was made by matching peak retention times of standard materials. These results are summarized in Table VI.

TABLE VI
TENTATIVE IDENTIFICATION OF PYROLYSIS
PRODUCTS OF ISOCYANURATE FOAM 8-A

COMPOUND	PYROLYSIS TEMPERATURE °C
C Cl ₃ F (blowing agent)	> 100
2,4, 6- Trimethyl (diethylaminomethyl) phenol (Catalyst)	> 100
Water	> 100
Acetonitrile	> 250
Acrylonitrile	> 250
Benzene	< 500 trace, > 500 Detection
Pyrolidone	< 500 trace, > 500 Detection
Pyridine	< 500 trace, > 500 Detection
Phenylisocyanurate	< 500 trace, > 500 Detection
Toluene	> 500
Styrene	> 500
Cumene	> 500
Aniline	> 500
Tolunitrile	> 500
p-toluidine	> 500

Figures 17 through 21 are photographs of the pyrolysis curves obtained using simultaneous thermal conductivity and flame ionization detectors at pyrolysis temperatures of 250, 380, 500, 850, and 1000°C. These temperatures were preselected after examination of the TGA curves (Figure 15). The use of a Hewlett-Packard Mini-prep accessory would permit collection of resolved or composite fractions. Confirmation of chemical identity of the isolated fractions could be accomplished using infrared spectroscopy and mass spectrometry.

D. EVALUATION OF THE FLAMMABILITY CHARACTERISTICS OF ISOCYANURATE FOAM

1. GENERAL

Flammability characteristics are those properties which describe the behavior of a material in simulated or actual fire exposure. A number of laboratory procedures were used in this study to classify these characteristics.

2. PRECONDITIONING OF TEST SPECIMENS

For the ASTM D-1692 and Bureau of Mines Penetration tests described below, samples of isocyanurate foams and foam systems were preconditioned prior to testing in a modified bell jar for a 72-hour period prior to testing at 50% relative humidity and 22°C. The humidity was controlled by a 141 ml solution of 43.0 percent sulfuric acid. This preconditioning procedure assured that all samples would have a uniform moisture content during the evaluation period. The bulk density of the uncoated isocyanurate foam ranged from 0.032 to 0.040 gm/cm³ (2.0 to 2.5 lbs./ft.³). The maximum moisture gain recorded for the uncoated foams was 3.65 percent by weight.

3. EASE OF IGNITION - HLT-15 INTERMITTENT FLAME TEST

This simple but relatively severe laboratory test provides an indication of the relative ease of ignition and propagation of materials. The specimen is suspended in a vertical position so that the heat of combustion will be carried upward by convection along the length of the specimen. (See Figure 22.) In addition the specimen is ignited five times using increasingly longer ignition periods. The sequence of ignition times and flame withdrawals are given below:

<u>Flame Application</u>	<u>Ignition Time</u>	<u>Burner Withdrawn</u>
1	5 Seconds	10 Seconds
2	7 Seconds	14 Seconds
3	10 Seconds	20 Seconds
4	15 Seconds	30 Seconds
5	25 Seconds	50 Seconds

In rating a composition, fire specimens 8" x 1/2" x 1/8" are burned. If the flame is extinguished within the period that the burner flame is withdrawn, the specimen has passed the ignition test. Each of the five test ignitions successfully passed is worth 20 points toward the rating for that specimen. An average is taken of the ratings for the fire specimens evaluated.

Table VII presents the results obtained in the evaluation of ease of ignition and flame propagation of the isocyanurate foams and foam systems. Figure 23 shows the differences observed when samples of the uncoated isocyanurate foam, the Fluorel-coated foam, and the foam protected by the intumescent coating were subjected to the HLT-15 test method.

TABLE VII
HLT-15 TEST RESULTS - ISOCYANURATE FOAMS AND FOAM SYSTEMS

Sample	Percent Weight Loss	Rating
Isocyanurate Foam	4.85	100
Fluorel-Coated Isocyanurate Foam	5.35	100
Intumescent-Coated Isocyanurate Foam	22.5	100

The uncoated isocyanurate foam had the minimum weight loss while the intumescent-coated foam showed excessive loss of weight during the HLT-15 test study. The fluorel-coated isocyanurate foam had a weight loss similar to that observed for the control sample. All three materials received an excellent rating by this test.

4. IGNITION AND FLAME PROPAGATION - ASTM D-1692

The ASTM D-1692 small-scale laboratory test has been used to determine the ignition and flame propagation of plastic materials. However, it is not a severe test. Apparatus for the ASTM D-1692 test was revised to overcome problems affecting reproducibility and to permit the testing of foam samples at horizontal, vertical, or 45° angle positions. The recommended inner cone flame height of 0.25 inch was achieved with a Terrill burner. Uniform positioning of the burner flame was achieved by constructing a burner slide track at the base of the ring stand used to support the

sample. A considerable effect of draft across the isocyanurate foam samples was observed when the tests were conducted in the hood with varied ventilation. Therefore, a test housing was constructed which consisted of a transite box 1' x 2' x 2' high with a one-inch opening around the bottom, an open top, and a front viewing window. Final control of the draft was achieved by adjusting and partially sealing the hood control slat to obtain a draft just sufficient to carry away the pyrolysis and combustion gases.

Table VIII presents the summary of results obtained for the uncoated isocyanurate foam and isocyanurate foam systems in the ASTM D-1692 test. In the horizontal position, all three materials rated as self-extinguishing, although the intumescent-coated foam was on the border line, all three materials burned slowly in the horizontal position.

Figure 24 is a photographic composite showing char length and sample distortion after evaluation by the ASTM D-1692 test procedure in the horizontal, 45° angle, and vertical positions.

Additional studies of the ignition and flame propagation characteristics of the isocyanurate foam and coated foam systems are summarized in Table IX.

5. OXIDATIVE DEGRADATION AND CHAR FORMATION

Results for the uncoated foam are presented here. Results for the two types of coatings are presented in Sections VI and VII below.

a. Air Oxidation

Figure 25 is a composite illustration of the oxidative degradation of isocyanurate foams in a temperature range of 20-300°C. Figure 26 is a similar composite illustration of the oxidative degradation of

TABLE VIII

ASTM D-1692 FLAMMABILITY TEST RESULTS - ISOCYANURATE FOAM AND FOAM SYSTEMS

Sample	Sample Position	Self-Extinguishment Time (Seconds)	Average Charred Distance (Inches)
Isocyanurate Foam	Horizontal	35 - 55	0.51 ± 0.13
Isocyanurate Foam	45°	45 - 60	3.31 + 1.14 - 0.83
Isocyanate Foam	Vertical	35 - 50	3.89 ± 0.10
Fluorel Coated Isocyanurate Foam	Horizontal	25 - 30	0.4 ± 0.10
Fluorel Coated Isocyanurate Foam	45°	30 - 37	2.00 ± 0.10
Fluorel Coated Isocyanurate Foam	Vertical	55 - 60	4.00 ± 0.15
Intumescent Coated Isocyanurate Foam	Horizontal	55 - 60	1.00 ± 0.05
Intumescent Coated Isocyanurate Foam	45°	50 - 55	2.5 ± 0.20
Intumescent Coated Isocyanurate Foam	Vertical	60	6 ± 0.00

TABLE IX
ASTM D-1692 - TEST RESULTS
(VERTICAL BURN)

Property	Specimen		
	Isocyanurate Foam (Control)	Isocyanurate Foam (Fluorel Coated)	Isocyanurate Foam (Intumescent Coated)
Initial Weight (grams)	11.7	8.7	24.0
Final Weight (grams)	<u>9.3</u>	<u>6.3</u>	<u>17.4</u>
Weight Loss (grams)	2.4	2.4	6.6
% Weight Loss	20.5	27.6	27.8
Density of Specimen (lbs/ft ³)	3.72	2.76	7.62
Time, seconds to burn:			
1 inch	7	10	10
2 inches	14	18	22
3 inches	22	30	33
4 inches	30	43	56
Maximum Char Length			
Top surface-inches	3.75	3.50	3.50
Bottom surface-inches	1.00	2.25	0.75

isocyanurate foams in a temperature range of 400-700°C. At a given exposure period of five minutes, the first char formation occurred at approximately 200°C. Moderate shrinkage was evident at 400°C. A highly flame-resistant boron-containing compound was observed to form at a temperature of 550°C or higher. This char greatly reduced the rate of flame penetration during actual exposure to a high heat flux fire (22 BTU/ft.²sec.).

b. Scanning Electron Microscope

The scanning electron microscope was used to follow the mechanism of oxidative degradation of the isocyanurate foam samples. Figures 27a and 27b show no effects of degradation following 5-minute exposure of test specimens to air at 100°C. Figures 27c and 27d show thermal stress and blistering of cell membranes following a five-minute exposure of test specimens at 300°C. Figures 28a and 28b show extended degradation of isocyanurate foams after 5-minute exposure at 500°C. Figures 28c and 28d show extreme stressing as well as actual fracture of the cell membranes.

Figures 29a - 29d show complete degradation of the cell membranes and carbonization of cell struts after 5-minute exposure at 550°C. Figure 30a shows the complete degradation of cell membranes and partial rupture of cell struts after a 5-minute exposure at 700°C.

Figures 30b and 30c show fracture of the cell struts and actual carbonization of the polymeric material. Figure 30d, a highly magnified section of the strut, shows the greatly increased porosity caused by the oxidative degradation process.

Finally an experiment was conducted to determine the effect of time

on the degradation of isocyanurate foams. Figure 31a shows the onset of stress in cell membranes after a 30-second exposure at 500°C. Figure 31b shows partial rupture of cell membranes after a 90-second exposure at 500°C. Exposure of the isocyanurate polymers for 300-seconds at 500°C. shows complete carbonization of cell struts and loss of membrane structure (Figures 31c and 31d).

c. I. R. Spectroscopy

Infrared spectroscopy was used in the preliminary investigation of the oxidative degradation of isocyanurate foams. KBr pellets were prepared from the char residue. The results of this study are displayed in Figures 32 through 36. Figure 32 is the infrared spectrum of the control isocyanurate foam as determined using a Beckman Model IR-8 Infrared Spectrophotometer.

The isocyanurate foam shows absorptions characteristics of N-H (3.00μ), -N=C=O (4.35μ), C=O (6.0μ) - (indicative of a urethane carbonyl), aromatic double bond (6.25μ) C-H (3.40μ), (6.75μ , and 7.20μ), C-O-R (9.7μ) and aromatic C-H (12.3 and 13.4μ). Oxidative degradation carried out at 200°C. resulted in a loss of intensity at 3.0μ , (this could be loss of water).

Oxidative degradation carried out at 300°C. shows loss of C-O-R intensity as well as loss of C=O. This is indicative of breakdown of the urethane moiety.

Further heating up to 700°C. shows complete loss of infrared absorption with the exception of -N=C=O at 4.35μ .

Further study is necessary in order to refine the analytical procedures using the KBr pellet technique or the attenuated total reflectance technique to resolve the detailed structural changes during the oxidative degradation studies.

Analysis of the infrared spectra shows little change in the overall isocyanurate structure below 200°C. Exposure to a heated environment at 300°C shows loss of isocyanate and isocyanurate structure. Infrared spectra of samples exposed to environments at 400 and 500°C show continued carbonization of the polymer structure which is in agreement with previous scanning electron microscope and visual observations.

d. I.R. Photography of Char Formation

Figure 37 is a composite photograph of infrared pictures showing progressive char formation of the uncoated isocyanurate specimens in an oxidizing flame at 1950°F. Figure 37a shows a slight charring at the leading edge. Figure 37b illustrates propagation of the char surface to a depth of approximately 3/4-inch after a two-second flame exposure. Figure 37c shows the surface char propagation to a distance of 1¼-inches after a four-second exposure. The leading edge of the sample has reached a temperature great enough to glow and show resistance to further char degradation. In Figure 37d the surface char may be observed to have propagated a distance of 1½-inches after an 8-second flame exposure. Figure 38 shows the progressive char formation on the foam surface after increasing flame exposure.

6. FLAME PENETRATION TEST - BUREAU OF MINES TEST

Fire endurance or flame penetration characteristics is a measure of the resistance of a material to "burn-through" when subjected to the direct impingement of an oxidizing flame. This property of a material is important for use in localizing a fire or providing protection in critical areas.

A schematic diagram of the apparatus for the flame penetration test is shown in Figure 39.

The flame temperature for each test sample run was measured by a chromel-alumel thermocouple which was referenced to the temperature of an ice bath using a Varian Associates Instrument Division Recorder (range of 50mv).

All samples of the specimen NASA isocyanurate foam sample 3a were tested for ten minutes while in direct flame contact. Two of the three test samples of NASA isocyanurate foam sample 6a were tested for ten minutes. However, to gain information about the maximum high-temperature flame resistance, the third sample was exposed until a burn-through was completed.

Table X lists information describing sample specifications and test conditions.

TABLE X
FLAME PENETRATION TEST - SPECIFICATIONS

Sample	Weight (gms)	Density (gms)	Flame Temperature (°F)	Test Duration (minutes)
3a-1	20.94	0.613	1959	10.0
3a-2	21.89	0.601	1916	10.0
3a-3	Flame Out - Test Discontinued			-----
6a-1	20.92	0.596	1926	10.0
6a-2	22.51	0.660	1916	10.0
6a-3	20.22	0.600	1959	18.35*

* Burn-through

Visual analysis of test samples is summarized in Table XI.

TABLE XI
FLAME PENETRATION TEST - SAMPLE ANALYSIS

Sample	Burn-Depth (Inches)	White Char Diameter-Inches	Black Char Diameter-Inches	Paper Scorch Diameter-Inches
3a-1	0.63	2.00	2.75	1.50
3a-2	0.41	2.75	3.20	1.00
3a-3	----- (Flame Out - Test Discontinued) -----			
6a-1	0.47	2.63	3.00	1.60
6a-2	0.44	2.70	3.20	1.50
6a-3	Burn-through	3.00	3.50	Burn-through

Figure 40 shows actual photographs of the flame penetration test on isocyanurate foam samples, while Figure 41 compares photographs of coated and uncoated foams.

An additional test was performed using the uncoated isocyanurate foam to determine the relationship between time of fire exposure and weight loss. Figure 42 shows the weight loss observed as a function of exposure time.

Finally, one test each to burn-through was run on the uncoated and the two-coated foams. The results are given in Table XII. The Fluorel-coated foam required the longest time to obtain a burn-through, although all three materials showed very good endurance, requiring longer than ten minutes for burn-through.

TABLE XII
FLAME PENETRATION - BUREAU OF MINES TEST

	Test Specimens		
	Isocyanurate Foam (Control)	Isocyanurate Foam (Fluorel Coated)	Isocyanurate Foam (Intumescent Coated)
Initial weight (grams)	28.6	22.5	31.6
Final weight (grams)	<u>24.9</u>	<u>19.8</u>	<u>29.2</u>
Weight loss (grams)	3.7	2.7	2.4
% Weight Loss	12.9	12.0	7.6
Burn-Through (Minutes)	24.0	31.25	18.25
<u>Diameter of Char</u>			
Front Surface, Inches	2.75	2.75	1.815
Back Surface, Inches	1.94	2.125	9.94

7. LIMITING OXYGEN INDEX

The Limiting Oxygen Index (LOI) Method developed by Fennimore, et.al.⁽⁹⁾ permits the assessment of the flammability hazard of a polymer as a function of ignition position and geometry of the sample. "Flame retardancy" is a term that has been used to describe the non-flame propagating nature of a "fuel" liberated from a substrate on heating, in any mixture ratio with the environment. In actual practice, most measurements are conducted

in air and, hence, flame retardance is conventionally associated with an environment containing 21% oxygen. The frequently observed contradicting behavior of many plastics which are rated flame-retardant by certain flammability tests, but flammable by others, can be traced to the fundamentally combustible nature of the "fuel" liberated in air. Many of the small-scale laboratory tests, which stipulate self-quenching times as a criterion for the rating, presuppose ignition and flame propagation by the substrate. Only inherently flame-retardant polymers fulfill the definition, i.e. they produce only non-combustible volatile gases on degradation in air. This is true of the highly cross-linked aromatic polymers or aromatic heterocyclic polymers possessing a high degree of resonance stability.

The LOI is defined as the minimum concentration of oxygen in nitrogen of which the combustion of a thin polymer rod can just be sustained in candle-type fashion. The LOI of a rod of isocyanurate foam was determined in this program. Figure 43 is a summary of the effect of oxygen concentration on the combustion of isocyanurate foam. A rather sharply defined LOI of 0.29 was observed. By this test, the isocyanurate foam would be judged as below average in flammability.

8. FIRE SIMULATION TESTS

A source capable of yielding a high heat flux was required in order to evaluate the thermal insulating quality of rigid cellular plastics. It was suggested that a JP-4/air fire could be created and controlled to yield conditions similar to that which exists under real fire conditions.

A combustion unit, similar to the one developed by NASA-Ames, was constructed and used to perform a comparative experiment on the isocyanurate

foams (see Figure 44). This thermal facility consisted of a firebrick-lined chamber of $\frac{1}{4}$ " steel plate sheet with a Ray Oil Burner, type 00 for mixing the fuel with air and injecting the mixture into the firebox. Air inlets placed in the bottom of the firebox were used to control the draft. Two 12" x 12" test areas were located on the top of the unit. Foam samples or a control plate containing a copper heat conduction bar for measuring the convection heat flux from the fire could be placed on either of these test areas. A gas sampling tube placed downstream of the test area was used to withdraw gas samples via an aspirator. Thermocouples placed inside the gas sampling port facilitated the determination of gas temperatures within the flame zone. Two hundred millimeter 304-stainless-steel gas sampling bottles were used to continuously withdraw samples for chemical analysis. Valves at each end of the sampling bottles were open during the test period. A septum placed at the midpoint of the bottles allowed for withdrawal of samples with a needle syringe.

A copper rod, $\frac{1}{2}$ " diameter and $3\frac{1}{2}$ " long was mounted inside a stainless steel bulkhead connector on the test area cover plate. Two constantan wires attached one inch apart formed two thermocouples. A copper wire from the top end of the bar was used to complete the circuit. The measured gradient along the bar and the known thermal conductivity of the bar were used to compute the heat conducted from the flame zone. Heat fluxes determined this way varied from 9 to 22 BTU/ft.² sec at the sample exposure area. The highest heat flux observed was produced at a JP-4 fuel flow rate of 1.5 gallons per hour. Measured flame temperature ranged from 1116°F to 1900°F depending on the rate of fuel flow.

Figure 45 presents the back surface temperature rise for the Fluorel-

coated isocyanurate foam, a sample of the isocyanurate foam coated with the NASA intumescent coating, and the control isocyanurate foam. The latter results were plotted from data obtained from NASA.

One run was made in the Fire Simulation Chamber with an uncoated isocyanurate foam block to obtain gas samples and to determine the surface response of the foam. The foam formed a uniform black char over the surface exposed to the JP-4 combustion flame. On cooling, the charred surface cracked badly. However, the structural integrity of the foam was maintained throughout the actual exposure. In this run, samples of gas downstream of the foam sample were withdrawn after one and five minutes exposure times. These samples were processed through a Hewlett-Packard gas chromatograph using a 20-inch silica-gel column ($\frac{1}{4}$ -inch diameter) in series with a 20-foot molecular sieve column (90% mal sieve 13 x + 20% mal sieve 5A) with helium flowing at 30 ml/min. On a water-free basis, the gas composition was determined to be essentially identical to that obtained with no foam present, as described in Section IV above. The volume of JP-4 combustion gas was sufficiently greater than the additional gas effluent volume from the foam that the possible quantities of additional gas species were undetectable.

9. COMPRESSIVE STRENGTH

An Instron tensile testing apparatus was used to determine the compressive strength of isocyanurate foam and coated foams. The nominal 2-inch cube samples were first allowed to equilibrate in the Instron Cabinet at selected temperatures. They were then subjected to compressive

loading using a strain rate of 0.1 inch/minute at the selected temperature. Figure 46 shows the results for isocyanurate foam over a temperature range of 50°F. to 450°F. at 50°F. intervals. The compressive strength appears to decline gradually as the temperature is increased. A second series of tests were conducted at 150°F. on each of the three materials. The compressive strength values measured were:

Uncoated foam:	18.2 psi
Fluorel-coated foam:	20.6 psi
Intumescent-coated foam:	24.2 psi

As might be expected, at temperatures below the initiation of substantial pyrolysis, the presence of the coatings tended to enhance the compressive strength.

E. LABORATORY ANIMAL EXPOSURE TESTS - LD-50 TESTS

1. GROSS EFFECTS

In experimental toxicology it is common practice to determine the quantity of poison per unit of body weight of an experimental animal which will produce a lethal effect. A commonly used measure in experimental industrial toxicology is the amount of exposure which is required to kill one-half of a group of experimental animals. This is known as the LD50 test (Lethal Dose-50 Percent) representing 50 percent fatalities.

The Manufacturing Chemists Association bases its definition of the term "poison" on this test. One of the definitions employed reads as follows "Poison - a substance or group of substances which produces death within 14 days in half or more than half of a group of 10 or more laboratory white rats weighing 200-300 grams, when inhaled continuously for a period of one hour or less at an atmospheric concentration of 200ppm or 2 milligrams or less per liter of gas, vapor, mist, or dust provided such concentration is likely to be encountered by man when the substances are used in any reasonable foreseeable manner."

A series of experiments were performed to determine the gross effects of isocyanurate foam, Fluorel-coated isocyanurate foam, and isocyanurate foam protected with the intumescent coating on the life of laboratory animals.

Male Sprague Dawley rats were exposed to the pyrolysis and degradation products which were generated by heating weighed samples of the isocyanurate foams and foam systems. These tests were performed in the Animal Exposure Chamber illustrated in Figure 5. The results are summarized in Table XIV.

TABLE XIV
EFFECT OF ISOCYANURATE FOAM PYROLYSIS
PRODUCTS ON SPRAGUE-DAWLEY RATS

<u>Number of Rats Exposed</u>	<u>Number of Rats Surviving 10-Minute Exposure</u>	<u>Material Weight</u>	<u>Initial</u>	<u>Weight of Rats (gm)</u>				
				<u>1 Day</u>	<u>2 Day</u>	<u>3 Day</u>	<u>4 Day</u>	<u>14 days</u>
4	4	1 gm	352	350	348	356	368	382
			390	375	381	383	397	405
			350	347	347	352	365	370
			340	340	340	346	355	367
4	4	1.1 gm	355	355	361	372	378*	394
			420	421	422	427	428	435
			360	371	372	377	387	388
			350	355	364	368	366*	375
4	0	2.0 gm	400 (DOR) ²					
			380 (DOR)					
			390 (DOR)					
			380 (DOR)					
4	4	9.0 gm 2.5 min. Exposure	389	410	398	396	414	438
			370	380	372	376	382	392
			350	365	352	359	369	382
			345	370	369	369	378	377

* This group of rats was not grooming themselves. Soft feces noted.

1. This test was terminated early due to the strange reaction of the rats. The rats would certainly have died if the test had been continued to the full 10-minutes exposure time used in all other tests.

2. DOR, Dead on removal from the chamber after 10-minute exposure period.

These results indicate that a ten-minute exposure to a concentration of 2.0 gm/ft.³ resulted in a 100 per cent death rate. However, at 1.1 gm/ft.³ all of the animals survived and appeared to have suffered no ill effects from the exposure as indicated by their constantly increasing weights during the two weeks following exposure. However, a severe reaction which included erratic muscular spasms was noted in all test animals during the exposures. The reaction was severe and was not noted with the fluorel refset nor with the 45-B-3 coatings. Additional tests at less than LD-50 conditions are merited to determine possible injury to the animals and to determine the pyrolysis products responsible for this behavior. When combined with the effects of other gases, as from a coating, possible adverse synergistic responses may be noted. From the data in Table XIV, actual LD-50 concentrations lie between 1.1 and 2.0 gm/ft.³

2. PHYSICAL COORDINATION AND RESPONSE

While the first phase of the study dealt with gross survival of animals subjected to products from burning polymers, long-range effects of these products on animal response and behavioral patterns are also of interest. One test to determine effects of toxic gases at less than lethal doses involves the animal's loss of equilibrium. This test is depicted in Figure 47, and involved a one-inch bar rotating at 5-rpm. In Figure 47a, several rats are shown prior to exposure to toxic gases. They are capable of staying on the rotating bar for several minutes. Some animals fall before duration of the 5-minute test, but only when trying to get off the bar, as illustrated by the rat in the center of the bar in Figure 47a. This rat is trying to climb the barrier, which

separates test animals, and fell shortly after this photograph was taken. However, this type of failure to pass the 5-minute test is easily distinguished from an animal falling due to inability to maintain equilibrium on the bar. The first adverse effects of toxic gases are readily distinguishable when animals are exposed to less than toxic concentrations, because of the obvious loss of physical coordination.

A variation of this test involves exposing animals while on the rotating bar. This variation is illustrated in Figures 47b, 47c, and in Figure 47d where one of the test animals is shown falling.

The Animal Coordination Chamber, just described, was used to evaluate post fire-exposure coordination in those rats surviving the initial LD-50 tests. Table XV summarizes the animal response measured 18 hours after fire exposure. No loss of physical facilities, as determined by this test, was noted for those animals surviving exposure to uncoated isocyanurate pyrolysis products.

While the experimental parameters have not been finalized, preliminary data suggests that use of this test in future testing is merited, especially when testing at less than lethal doses of toxic gases.

VI. INTUMESCENT COATING, 45-B-3

The previous section includes studies made on intumescent-coated isocyanurate foam. In this section, results for just the intumescent-coating are presented. In addition, oxidative degradation and char formation results for coated foam are discussed.

A. SMOKE DEVELOPMENT

Using a modified XP-2 chamber, light obscuration measurements were obtained on intumescent coating for conditions of no air flow and air

TABLE XV
ANIMAL RESPONSE - 18 HOURS POST FIRE EXPOSURE

Exposure Conditions	Ability to Pass 5-Minute Equilibrium Test				Remarks
	Animal # 1	Animal # 2	Animal # 3	Animal # 4	
Uncoated Isocyanurate Foams					
1.0 grams	P	P	P	P	
1.1 grams	P	P	P	P	
2.0 grams	D	D	D	D	
Fluorel-Refset					
1.5 grams	P	P	P	P	
2.0 grams	F*	F*	F*	F*	
2.8 grams	D	D	F	F	
3.0 grams	D	D	D	D	
Intumescent Coating					
2.0 grams	P	P	D	P	
4.0 grams	D	F*	D	D	
8.2 grams	D	D	D	F*	
JP-4 Fuel					
1.0 ml	P				
2.0 ml	P				
4.0 ml	D				

P Passed - 3 minute test on bar

D Died prior to testing

F Failed - 3 minute test on bar

F* Hind legs paralyzed, unable to grip bar - can walk with difficulty

Additional studies are required to determine specific response to pyrolysis and combustion effluents.

flow at 10cfm. The results are plotted in Figure 48. As with the coated-foam samples, smoke was more severe with air flow than without. Approximately 60 to 70% light obscuration occurred in one minute. Compared to the coated-foam results shown in Figure 13, the results for the unsupported coating shown in Figure 48 show just slightly less light obscuration for no air flow conditions.

B. FLAMMABILITY CHARACTERISTICS

Some results on intumescent-coated foams, which were not presented in the previous section are included here.

1. OXIDATIVE DEGRADATION AND CHAR FORMATION

a. Air Oxidation

Figure 49 is a composite illustration of the oxidative degradation of isocyanurate foams coated with intumescent coatings covering a temperature range of 20⁰C. to 300⁰C. Figure 50 is a similar composite illustration of the oxidation degradation of the coated isocyanurate foams for the temperature range of 400⁰C. to 550⁰C.

All samples were permitted to equilibrate for one day at 70⁰C. and 50% RH. The samples were then placed in an air-muffle furnace for a period of five-minutes at the preselected temperature. Figures 49a and 49b show little evidence of change when the control specimen is compared to the specimen exposed to 100⁰C. Onset of the intumescent reaction may be observed in Figure 49c after exposure of the test specimen to a temperature of 200⁰C. Further development of the char structure may be observed in Figure 49d (300⁰C. exposure). Shrinkage of the intumescent char structure may be observed in Figure 50 which illustrates the response to temperature exposures ranging from 400⁰C. to 550⁰C. For

comparison Figure 51 is a composite illustration showing the results obtained when isocyanurate foams coated with 45-B-3 were evaluated by the ASTM D-1692 test procedure. Figure 51a is a top view of test specimens; Figure 51b is an edge view of the test specimens.

b. Scanning Electron Microscope

The scanning electron microscope was used to follow surface changes during oxidative degradation of intumescent-coated isocyanurate foam. These photographs are shown in Figure 52.

Figure 52a shows the surface structure of the control intumescent coating as applied to the isocyanurate foam. Figure 52b shows the onset of the expansion of the intumescent coating after exposure at 200°C. Surface rupture was first observed in the intumescent coating after exposure at 400°C. (Figure 52c.) Continued degradation occurs at a temperature of 500°C. as shown in Figure 52d.

c. I. R. Spectroscopy

Potassium bromide pellets were prepared from intumescent-coated foam samples. However, after oxidative degradation, the foam substrate and the charred coating were difficult to separate, hence some C-N absorptions were found at about 4.2μ. Good separation of foam and coating was possible before the samples were heated, however.

Figures 53, 54, 55, and 56 are infrared spectra of the Ames Intumescent Coating removed from the isocyanurate foam before and after oxidative degradation. Figure 53, the control spectrum shows the characteristic bonds which have been assigned to the components of the intumescent coating. These bond assignments were divided into three categories - 1. polysulfide, 2. epoxide, and 3. the substituted

nitroaniline sulfuric acid. Prominent bonds attributed to the polysulfide-epoxy moiety included those at 7.1^{μ} , 7.7^{μ} , 8.0^{μ} , and 8.3^{μ} for the $\text{CH} - \overset{\text{S}}{\overset{\text{||}}{\text{S}}} -$ moiety. The bonds at 8.5^{μ} , 8.9^{μ} , 9.0^{μ} , 9.4^{μ} , and 9.9^{μ} are attributed to the $-\text{O}-\text{CH}_2-\text{O}-$ functional group. Absorption peaks at 6.1^{μ} , 6.3^{μ} , 6.4^{μ} , 6.8^{μ} , 15.5^{μ} , 16.0^{μ} are attributed to the nitroaniline -2- sulfuric acid constituent. Finally, the weaker bonds occurring at 6.7^{μ} , 10.9^{μ} , 12.1^{μ} , 13.4^{μ} , and 13.6^{μ} are attributed to the epoxide component. A minor bond at 4.3^{μ} is attributed to the $-\text{N}=\text{C}=\text{O}$ functional group, which resulted from incomplete removal of the underlying foam substrate.

Little change was observed in the infrared spectra prepared from the sample of intumescent coated foam exposed to air at 100°C . for five minutes. However, after exposure at 200°C . the major absorption bonds attributed to the above functional groups were not found. Further loss of absorption bonds found in Figure 55 are noted in Figure 56.

d. I. R. Photography

Figures 57, 58, and 59 are composite infrared photographs showing the formation of char on samples of isocyanurate foam coated with intumescent coatings. Evidence of char formation was seen as soon as the sample was placed into contact with the flame source. (See Figure 57a.) Continued edgewise char formation was observed in Figure 57b after a two-second flame exposure. Outgassing was first observed in the time period of 4 to 8-seconds with isolated char formation occurring approximately two inches away from the edges of the specimen as shown in Figures 57c and 57d. Continued intumescence was observed in Figure 58. A strong overall surface char was formed

24-seconds after sample contact with the direct oxidizing flame. Considerable outgassing and smoke development was observed during the char formation. Continued cracking of the char was observed as the intumescence continued, (Figures 59a and 59c). Smoke evolution from cracks emanating in the border region between the area of intumescence and the area of active char formation may be observed in Figure 58d. Once formed the expanded char structure provided an excellent barrier to further degradation.

2. FIRE SIMULATION CHAMBER TEST

An aluminum panel coated with 45-B-3 was tested in the fire simulation chamber burning JP-4 fuel by the procedure described in Section V-D above. Analysis of a gas sample from a location downstream of coated specimen gave essentially the same composition as quoted in Section IV-E above with no specimen present. The intumescent coating formed a very light-weight puffy char, which was approximately four to five inches high over the exposed surface. The aluminum backing plate was not greatly affected.

3. LABORATORY ANIMAL EXPOSURE

The animal exposure test procedures were previously discussed in Section V-E, and the apparatus shown in Figure 5.

Table XVI summarizes the effect of intumescent coating 45-B-3 pyrolysis products on male Sprague-Dawley rats.

The initial LD-50 dose is about 3 gm/ft.³, however the LD-50 based on the two week survival period is 2.0 gm/ft.³ All animals

TABLE XVI
EFFECT OF INTUMESCENT COATING 45-B-3 PYROLYSIS
PRODUCTS ON SPRAGUE-DAWLEY RATS

<u>Number of Rats Exposed</u>	<u>Number of Rats Surviving 10-Minute Exposure</u>	<u>Material Weight</u>	<u>Initial</u>	<u>Weight of Rats (gm)</u>				
				<u>1 Day</u>	<u>2 Day</u>	<u>3 Day</u>	<u>4 Day</u>	<u>14 Day</u>
4	3	2.0 gm	362	320	325	340	347	335* ²
			386	360	364	362	374	420
			376(DOR)* ¹					
			396	365	362	362	370	397
4	1	4.0 gm	385 (DOR)					
			398	371	355	344	326	* ³
			343 (DOR)		*partially paralyzed		progressive paralysis	
4	1	8.2 gm	408 (DOR)					
			410 (DOR)					
			372 (DOR)					
			385 (DOR)					
			399	362	Dead			

- 1.* Dead on removal from the chamber.
 2.* Died
 3.⁸ Died 11 days after exposure, wt. 199g.

exposed to pyrolysis products of 45-B-3 were dyed yellow from these gases and remained yellow for the subsequent four-week observation period.

Animal responses were also determined using the equilibrium test and are summarized and compared to the foam control and fluorel-refset in Table XV.

VII FLUOREL REFSET

In Section V, some studies on Fluorel-coated foam were presented. In this section, results for just the Fluorel coating are discussed. In addition, oxidative degradation and char formation results for the coated foam are discussed.

A. SMOKE DEVELOPMENT

The per cent light obscuration of unsupported fluorel refset is shown in Figure 60 for dynamic and static air atmospheres. The dynamic atmosphere resulted in initially higher obscuration values, however after 50 seconds both methods gave about the same results. Considerably less smoke was observed than with the coated foam shown in Figure 13 for static air conditions.

B. THERMAL ANALYSIS

Thermal analyses of fluorel refset coating were made using a Dupont Model 950 Thermogravimetric Analyzer and a Dupont Model 900 Differential Thermal Analyzer. Figure 61 presents the thermograms for samples of Fluorel which were subjected to a 10°C./min. dynamic heating rate in oxygen and nitrogen environments (100cc/minute flow rate). No differences were observed in the thermograms until the temperature exceeded 350°C. at which time the sample heated in the oxygen environ-

ment showed an acceleration of weight loss until a char yield of 40% was reached at approximately 400°C. A similar weight loss was observed to start at approximately 450°C. in the sample exposed to the inert nitrogen environment. A relatively stable char yield of 45% was observed to form at approximately 500°C.

Analysis of the differential thermal analysis thermograms shown in Figure 62 showed that an initial endothermic peak occurred at 350°C. followed by a strong exothermic response in the oxygen environment. The Fluorel sample, exposed to the nitrogen environment, exhibited two endothermic peaks, one at 270°C. and a second peak at 350°C. which was followed by a strong exothermic reaction at 475°C. A more detailed account of the chemical nature of these reactions is given in the next section covering analytical techniques.

C. CHROMATOGRAPHIC ANALYSIS

Separation of the pyrolysis products from Fluorel Refset was achieved using a 10' long x 1/4" diameter, stainless steel column packed with 50/80 mesh Porapak Q. Before use, the column was conditioned for 18 hours at 250°C with He flowing at 30cc/min. Carrier gas was helium flowing at 30cc/min. and 40 psig. The dual thermal conductivity Detector (TCD) was operated at 200mA and 250°C.

The following experimental sequence was used to pyrolyze 20 mg samples with the Hewlett-Packard Pyrolyzer attachment:

1. Insert pyrolysis probe and sample into 250°C injection port and condition 15 minutes.
2. Pyrolyze 15 sec. at 800°C and start analysis sequence.
3. Column Temperature Program -

- a. Hold 10 minutes at 80°C
- b. Increase the oven temperature at 6°C/minute to 250°C
- c. Hold 10 minutes at 250°C and cool for next sample.

When Fluorel Refset was pyrolyzed by the foregoing technique, a black residue was recovered, corresponding to 21 percent of the original sample weight. By contrast, when Fluorel Refset was heated in an air atmosphere, a white residue was obtained which was estimated at about 5-10 percent of the original sample weight. Exact weight was not determined because of difficulty of removal of the residue from the pyrolysis probe. Analysis of the residues resulting from both pyrolysis and oxidative degradation of Fluorel Refset was not carried out. Infrared and elemental analysis of these residues would be of value in determining the mechanism of Fluorel Refset decomposition.

A study of the thermograms obtained during oxidative degradation and pyrolysis of Fluorel-Refset indicated the first major weight loss occurred at 450°C. in the inert nitrogen environment (see Figure 61). A strong exothermic reaction was also observed in the inert environment in the same temperature region (see Figure 62).

Pyrolysis of Fluorel Refset, as described above, resulted in the separation of more than 28 peaks as shown in Figure 63. Tentative identification of twelve low molecular weight products was made by matching retention times of known compounds. These results are summarized in Table XVII. The total area under the 28 major peaks was determined and used to approximate the percentage of each peak. Included in Table XVII are the relative peak areas from the chromatographic output. Besides these compounds which were tentatively identified, relative peak areas for all other major peaks are tabulated.

TABLE XVII

RELATIVE QUANTITIES OF PYROLYSIS CHROMATOGRAM PEAKS OF FLUOREL REFSET

Peak Number	Relative Area	Percent Area	Tentative Identification
1	200,800	1.94	Carbon Monoxide, Oxygen, Nitrogen
2	2,286	0.02	Hydrogen Fluoride
3	320,000	3.04	Carbonyl Fluoride
4	10,270	0.098	Trifluoromethane, Hexafluoroethane
5	46,930	0.45	Difluoromethane
6	7,817,000	75.0	1,1-Difluoroethylene
7	22,400	0.22	Hexafluoropropene-1
8	6,214	0.059	-
9	34,520	0.34	Perfluorobutene-2
10	1,928	0.018	Perfluorobutene-1
11	19,290	0.18	-
12	39,260	0.38	-
13	222,000	2.12	-
14	70,120	0.68	-
15	44,480	0.43	-
16	54,250	0.52	-
17	60,980	0.54	-
18	70,240	0.67	-
19	92,890	0.89	-
20	109,200	0.96	-
21	169,800	1.63	-
22	67,830	0.65	-
23	66,720	0.64	-
24	90,450	0.86	-
25	194,400	1.86	-
26	168,300	1.61	-
27	54,560	0.52	-
28	<u>373,900</u>	3.58	-
TOTAL	10,423,438		

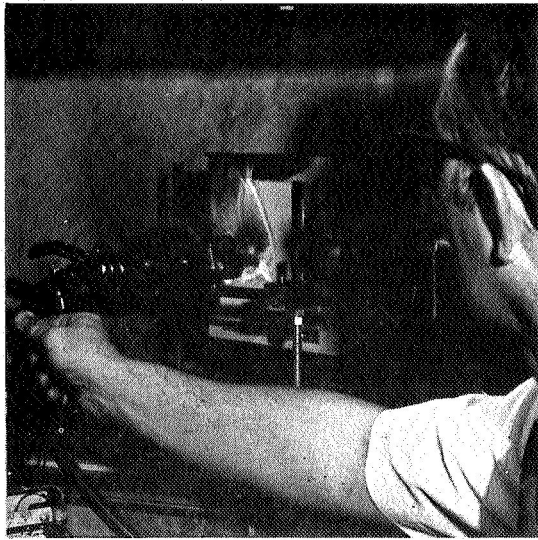


FIGURE 40a. IGNITION

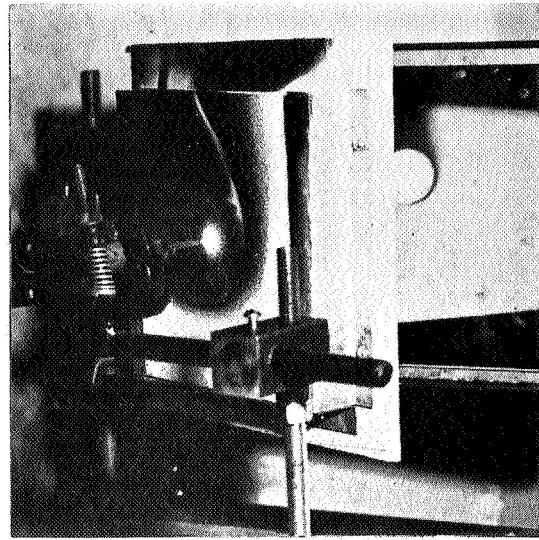


FIGURE 40b. 1 MINUTE
EXPOSURE

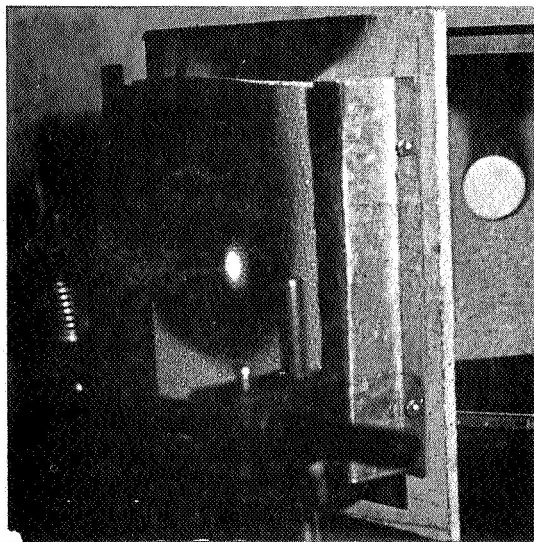


FIGURE 40 c. 10 MINUTE
EXPOSURE

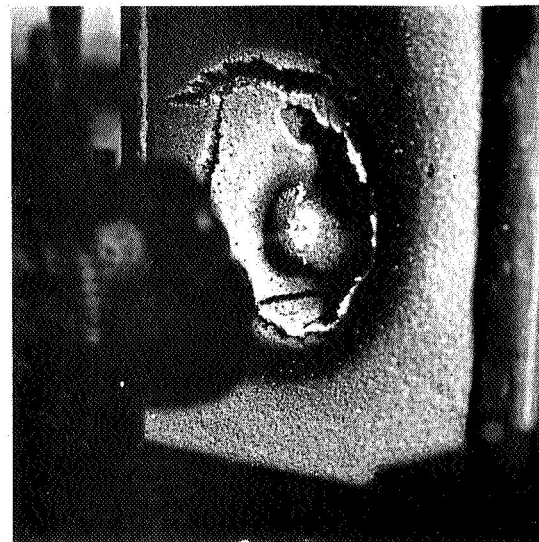


FIGURE 40d. 24 MINUTE
EXPOSURE

FIGURE 40. FLAME PENETRATION
TEST - ISOCYANURATE
FOAM

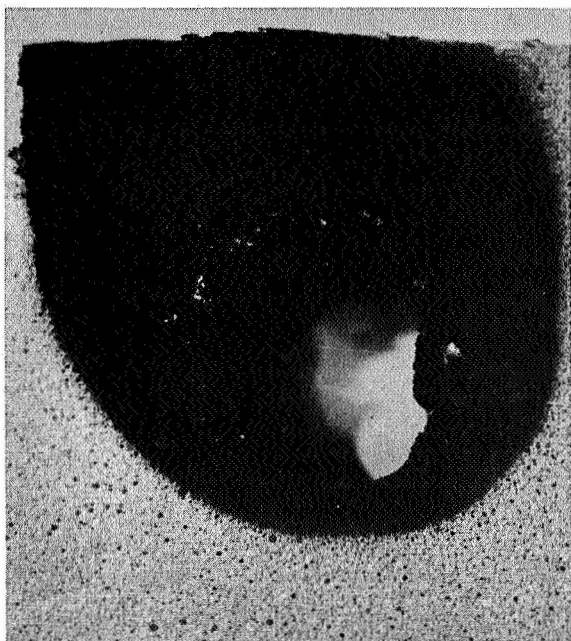


FIGURE 41a. FOAM

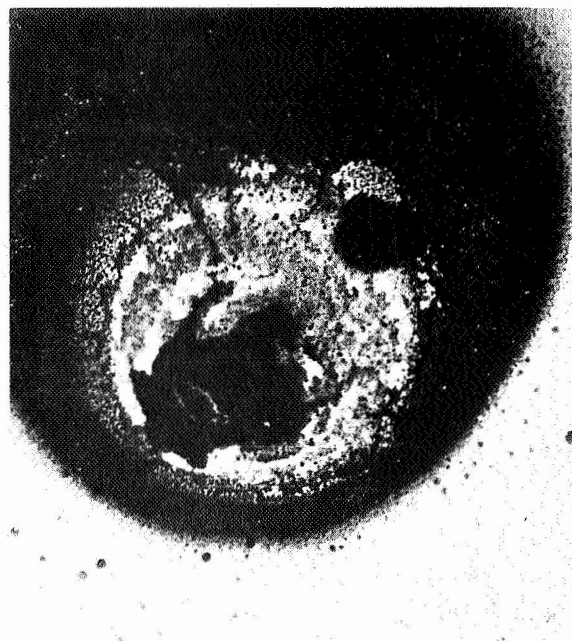


FIGURE 41b. FLUOREL
COATED FOAM

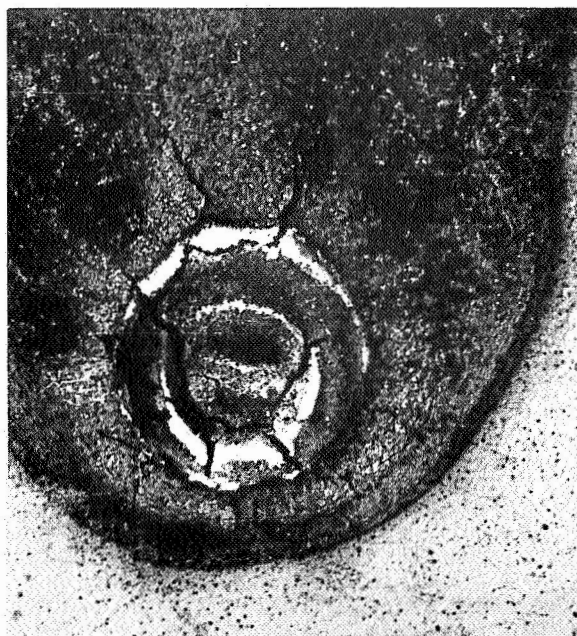


FIGURE 41c. INTUMESCENT
COATED FOAM

FIGURE 41. FLAME PENETRATION TEST
ISOCYANURATE FOAM AND FOAM
SYSTEMS

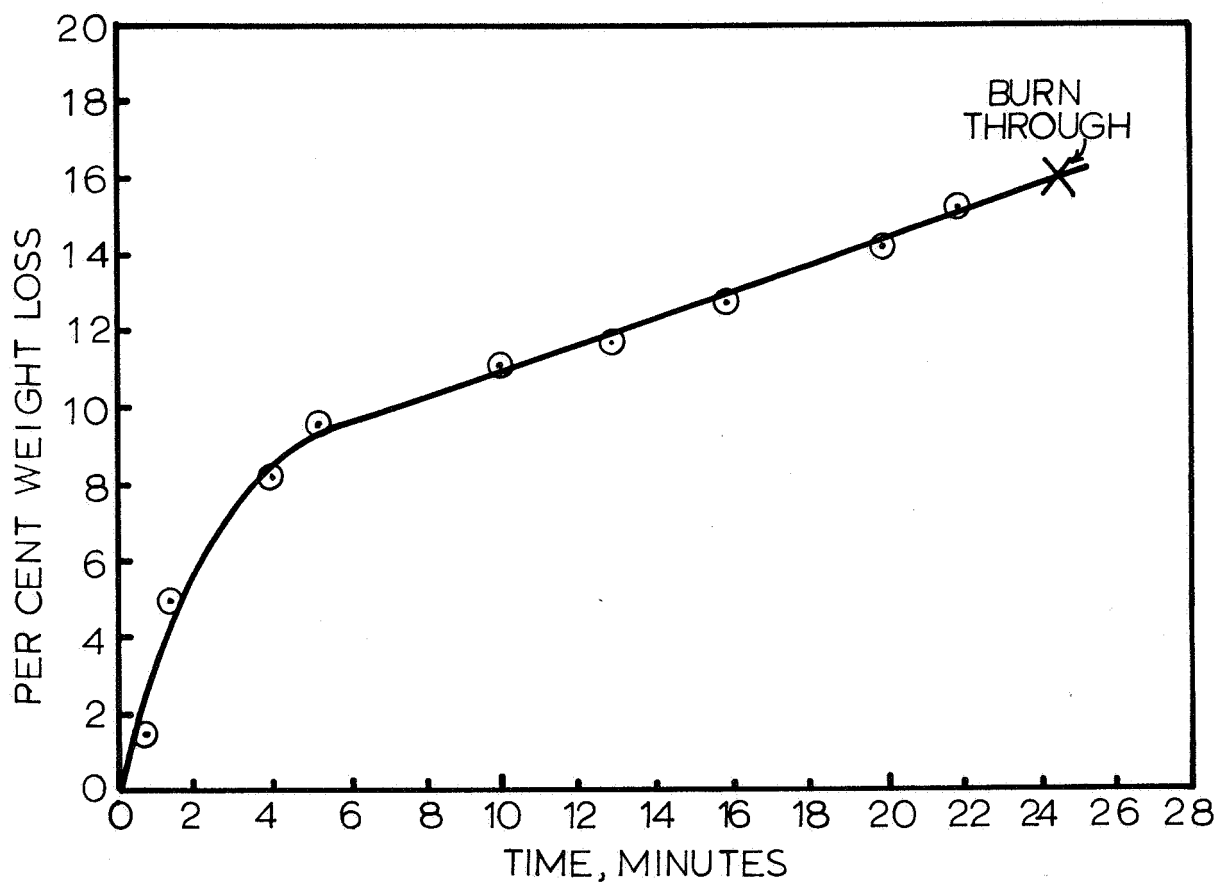


FIGURE 42. ISOCYANURATE FOAM —
WEIGHT LOSS vs EXPOSURE TIME

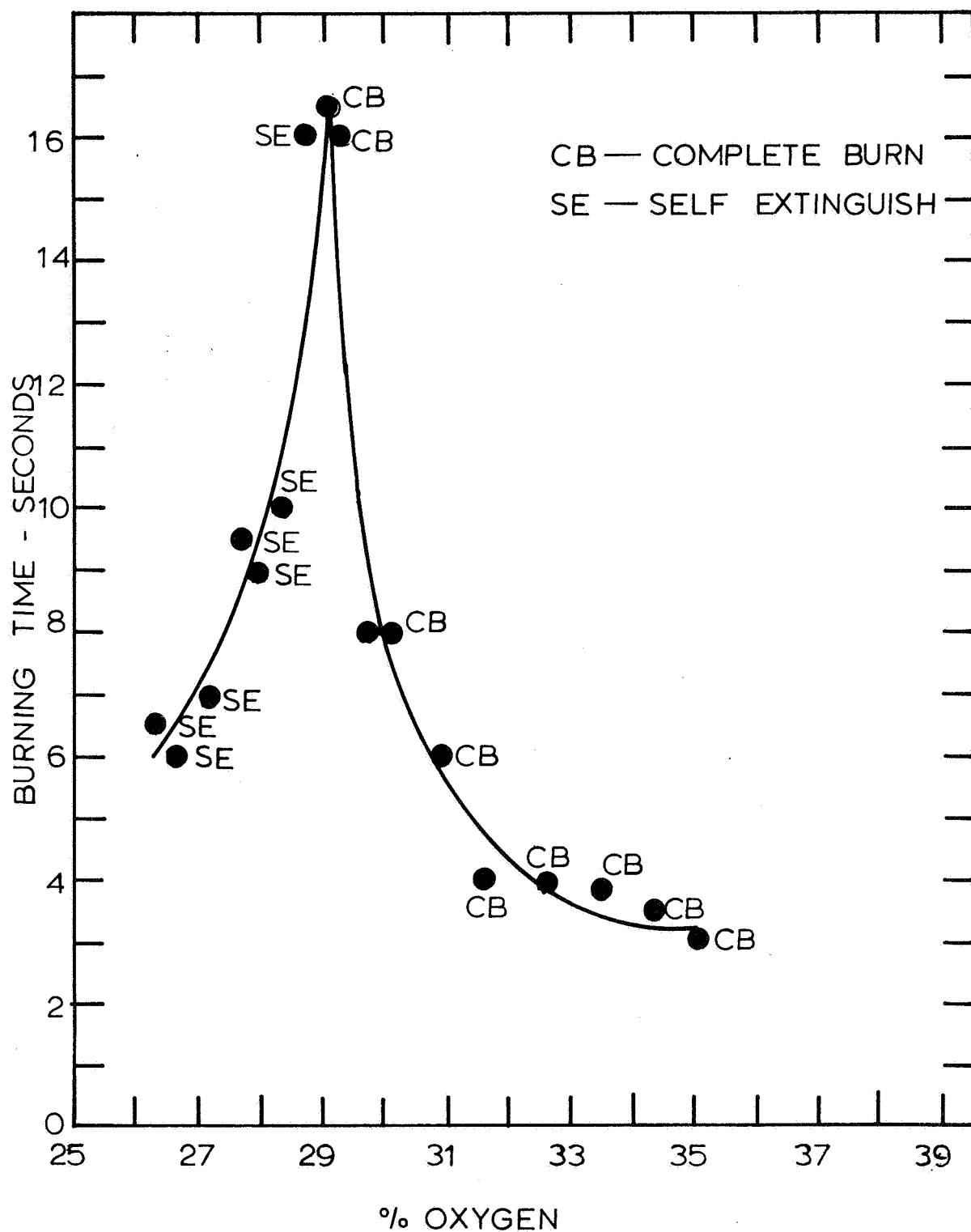


FIGURE 4.3. EFFECT OF OXYGEN ON THE COMBUSTION OF ISOCYANURATE FOAM

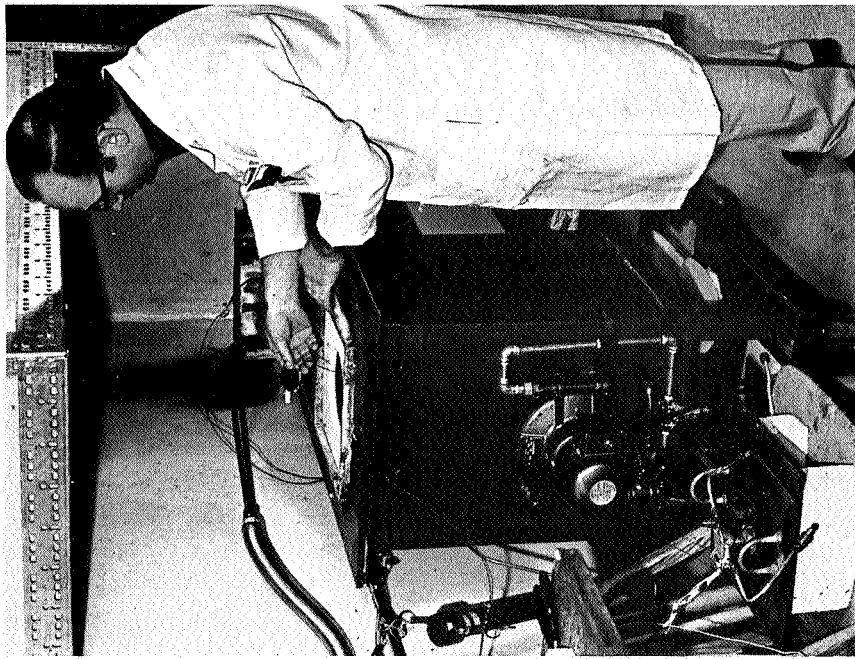


FIGURE 44 a FIRE SIMULATION
CHAMBER

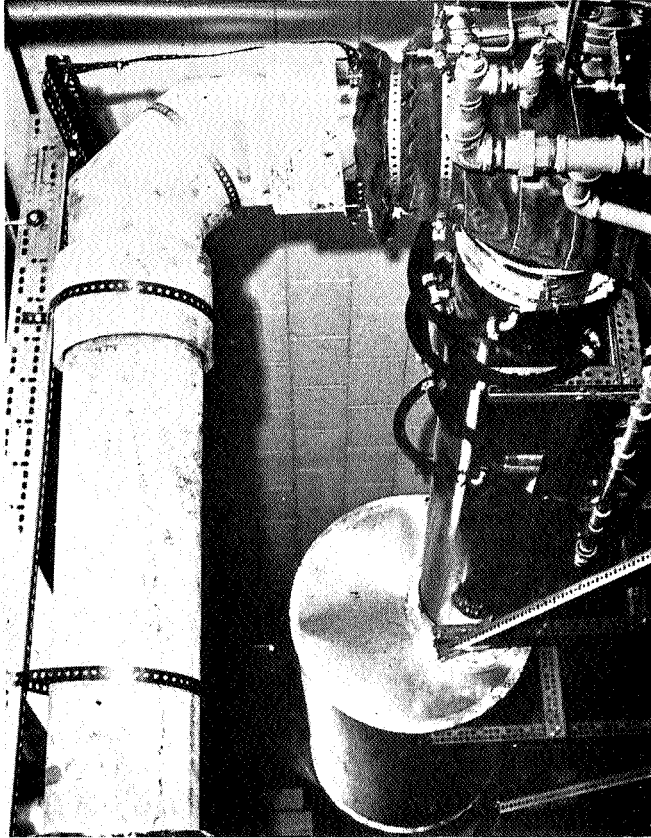


FIGURE 44b. EXHAUST DUCT AND
SCRUBBER

FIGURE 44. FIRE SIMULATION APPARATUS

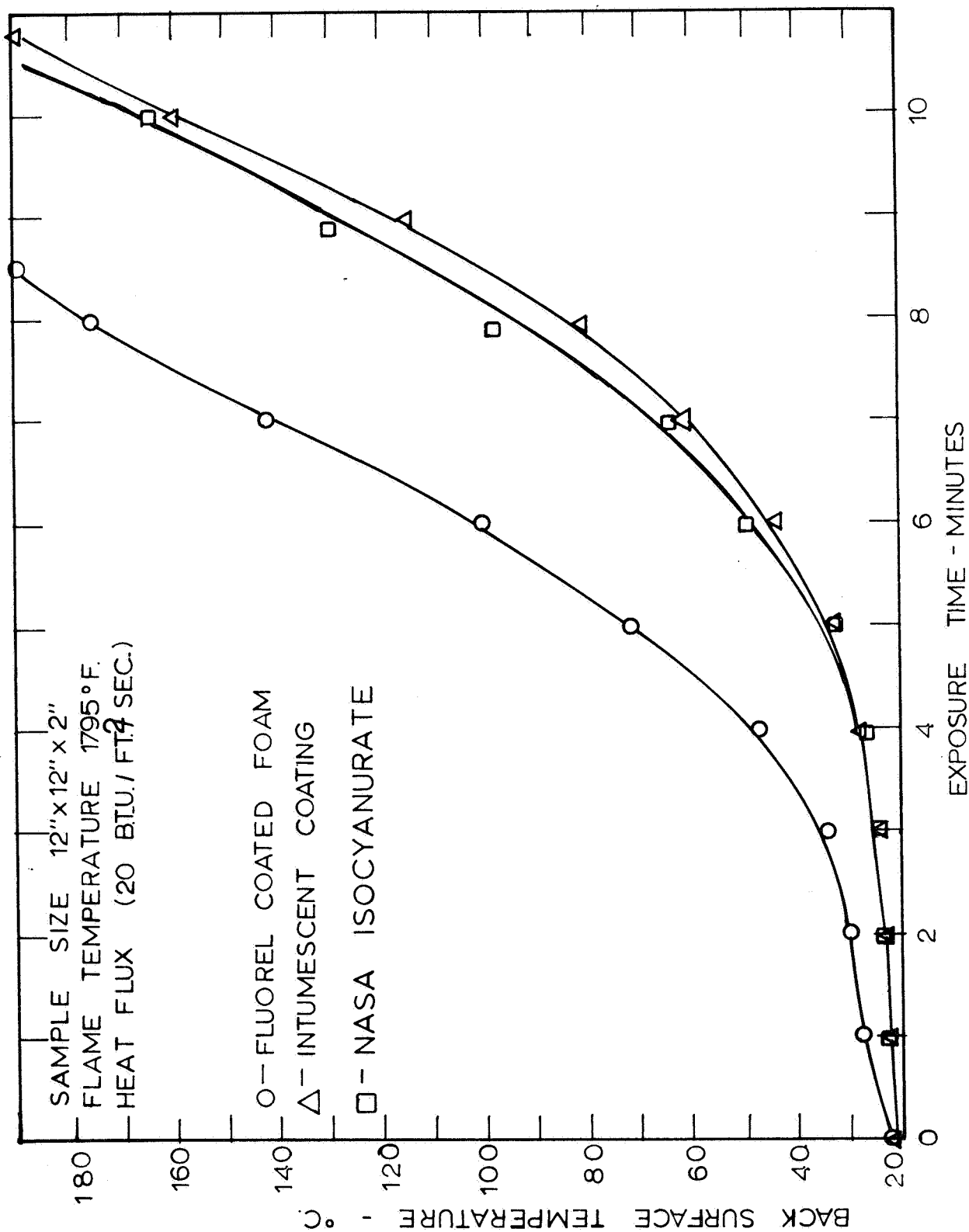


FIGURE 45. EFFECT OF COATING ON BACK SURFACE TEMPERATURE RISE

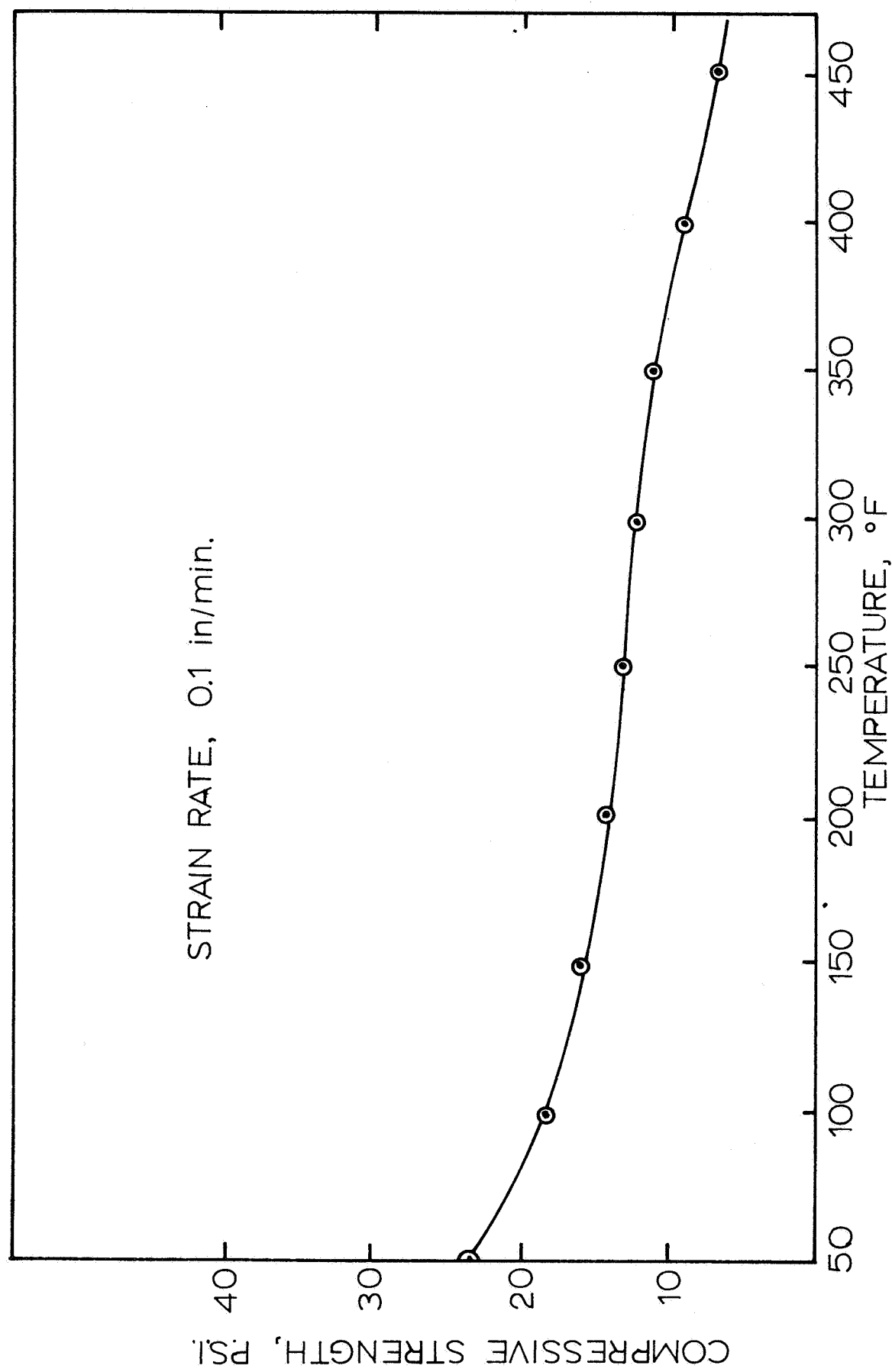


FIGURE 46. EFFECT OF TEMPERATURE ON THE COMPRESSION STRENGTH OF ISOCYANURATE FOAM AT 10 PERCENT STRAIN.

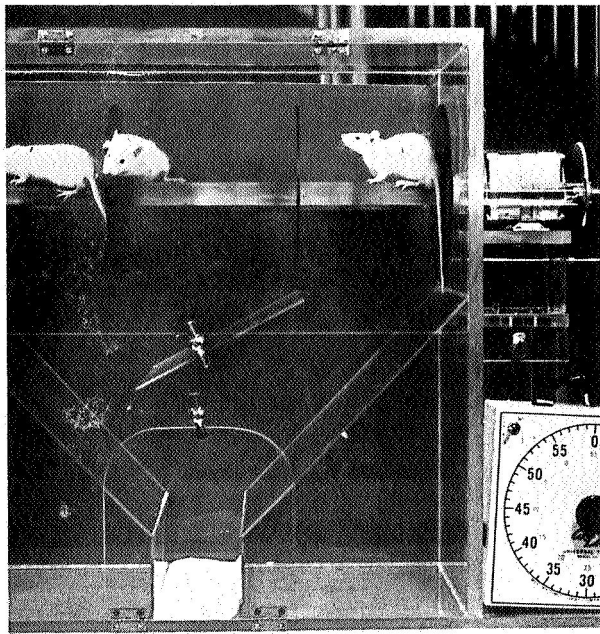


FIG. 47a. PRE-EXPOSURE

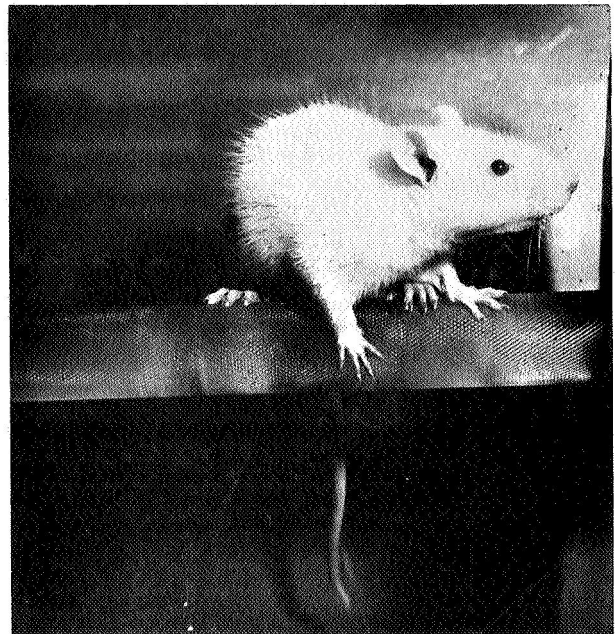


FIG. 47b. RESPONSE
EXPOSURE



FIG. 47c. RESPONSE
DURING EXPOSURE

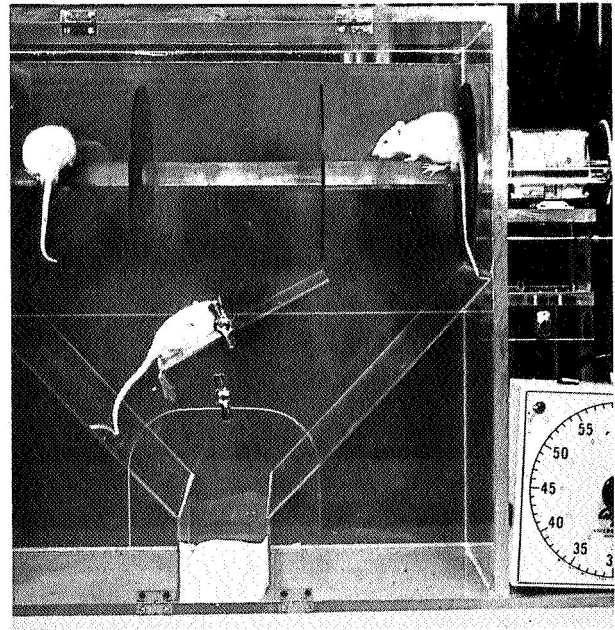


FIG. 47d. ANIMAL LOSS
OF STABILITY

FIGURE 47. ANIMAL RESPONSE CHAMBER

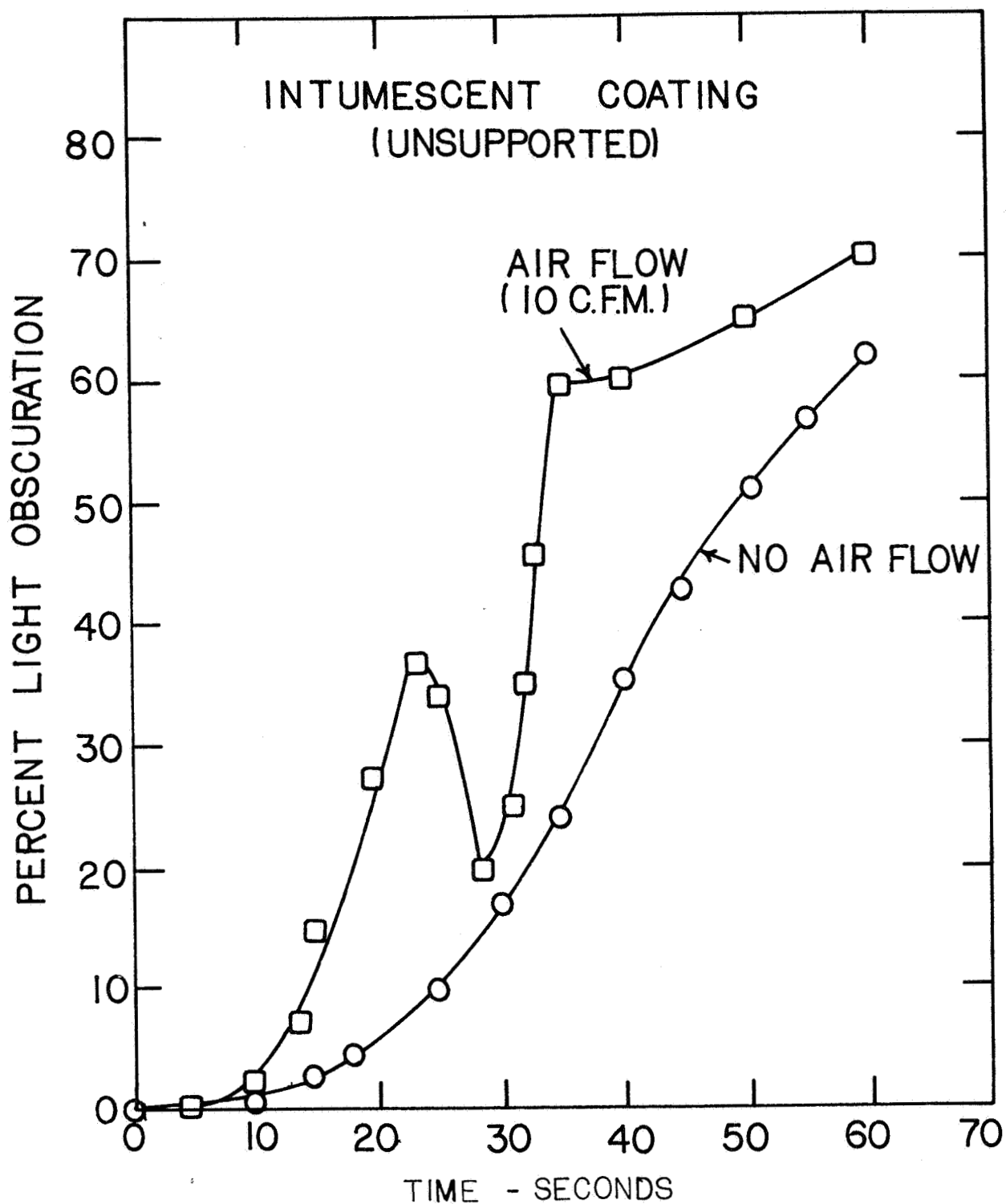


FIGURE 48. EFFECT OF COATING ON SMOKE DEVELOPMENT.

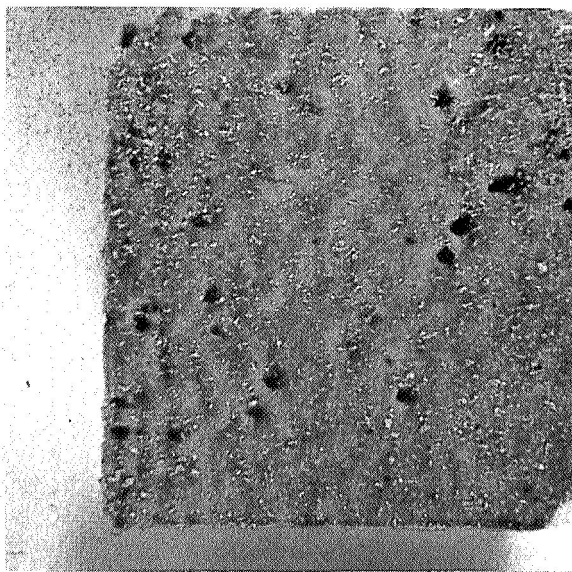


FIGURE 49a. CONTROL

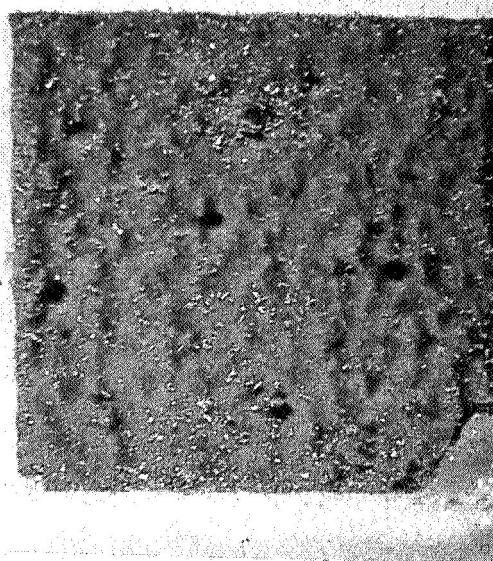


FIGURE 49b. 100°C.

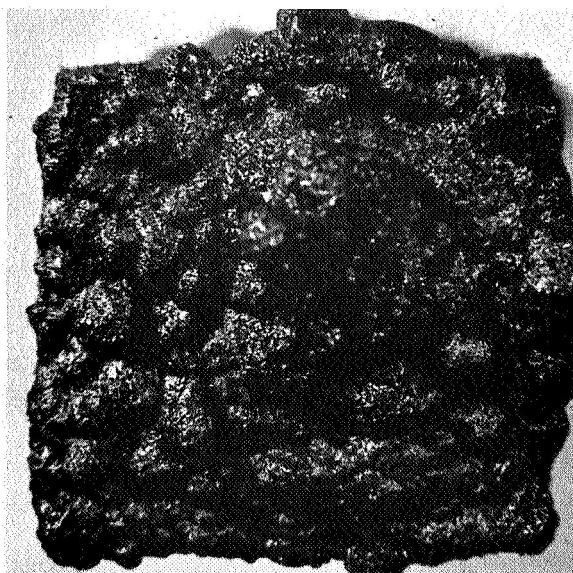


FIGURE 49c 200°C,

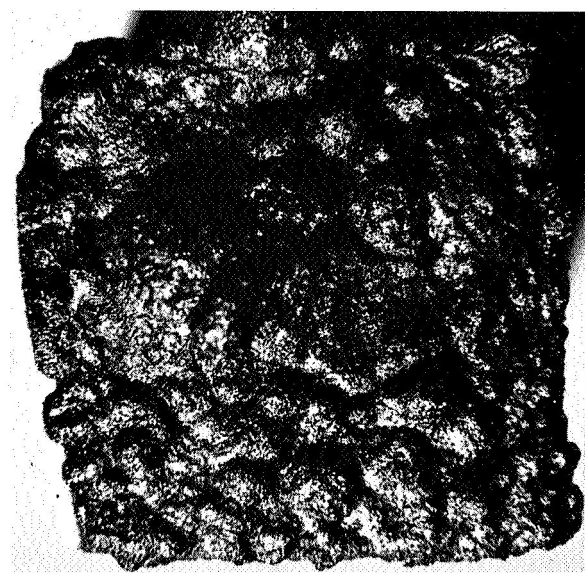


FIGURE 49d. 300 °C.

FIGURE 49. OXIDATIVE DEGRADATION OF
INTUMESCENT COATED
ISOCYANURATE FOAM

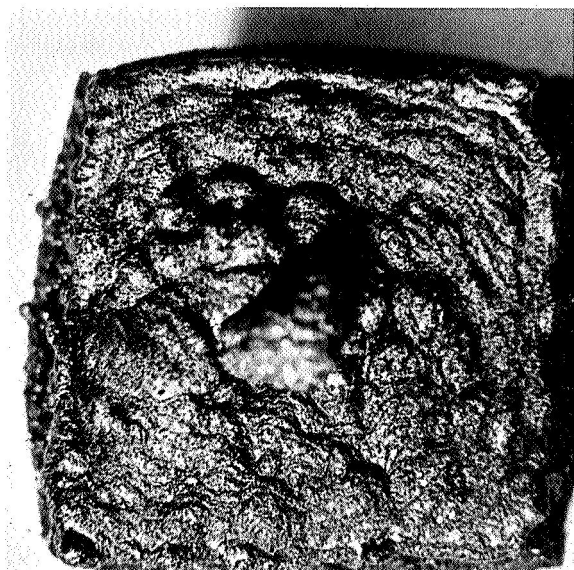


FIGURE 50a. 400°C.

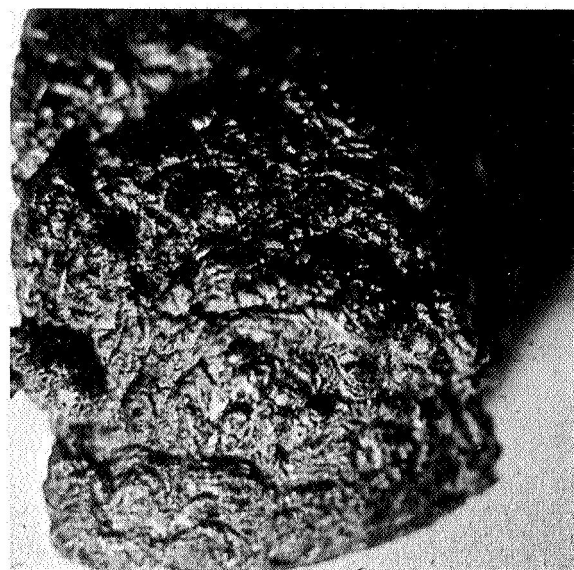


FIGURE 50b. 500°C.

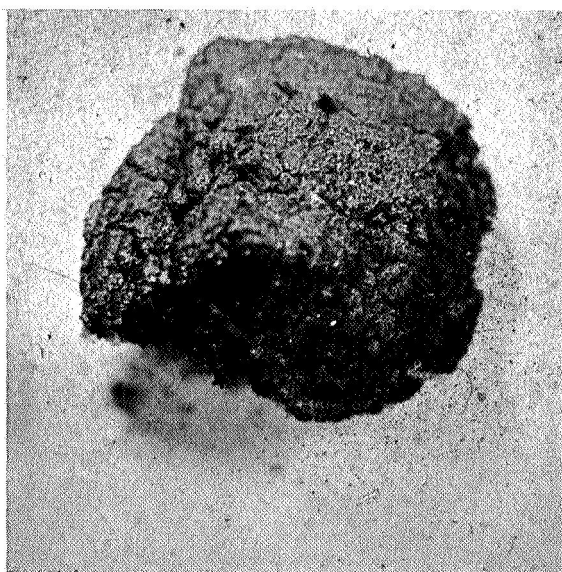


FIGURE 50c. 550°C.

FIGURE 50. OXIDATIVE DEGRADATION OF
INTUMESCENT COATED
ISOCYANURATE FOAM

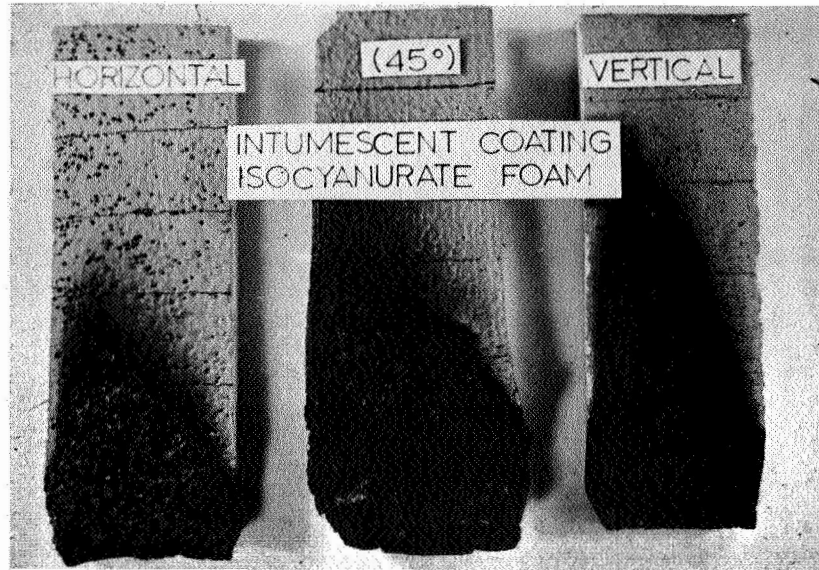


FIGURE 51 a. ASTM D-1692
(TOP VIEW)

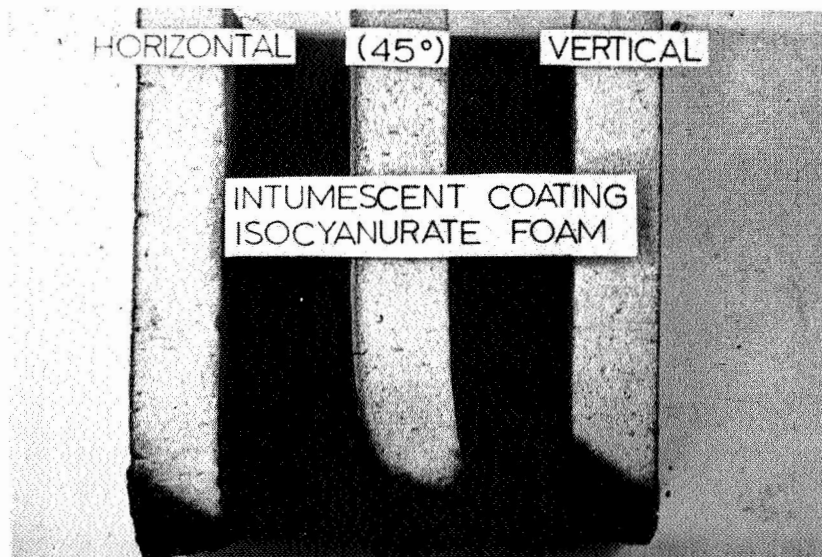


FIGURE 51 b. ASTM D-1692
(EDGE VIEW)

FIGURE 51. COMPOSITE - BURNED
SAMPLES - ASTM D-1692 TEST

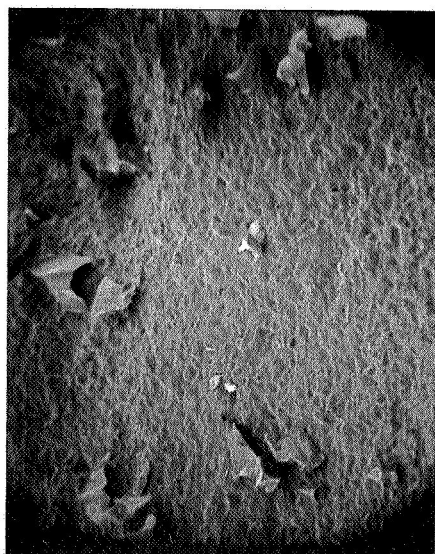


FIGURE 52a. CONTROL - 55X

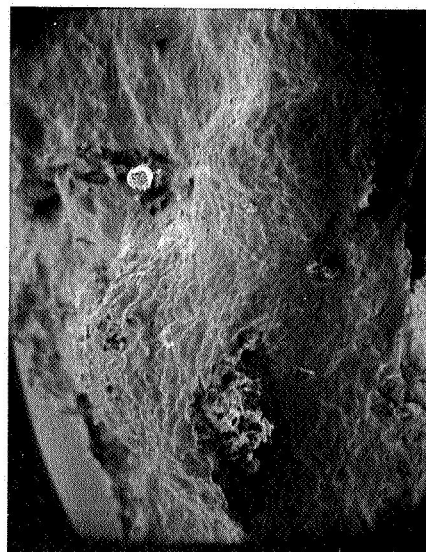


FIGURE 52b. 200°C - 20 X

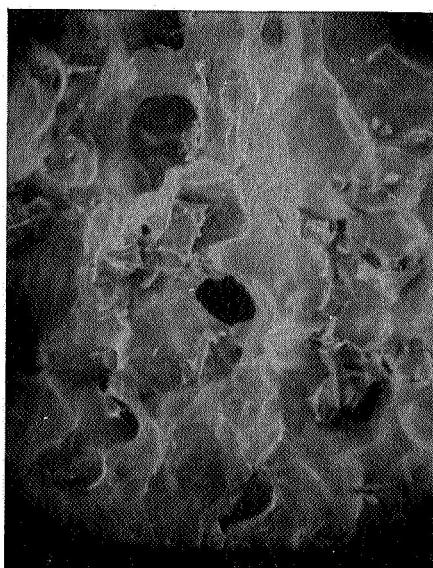


FIGURE 52c. 400°C - 48X

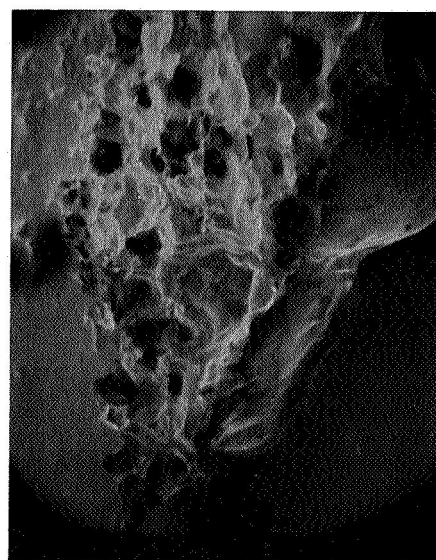


FIGURE 52 d. 500°C - 20 X

FIGURE 52. OXIDATIVE DEGRADATION OF
INTUMESCENT COATED ISOCYANURATE FOAM

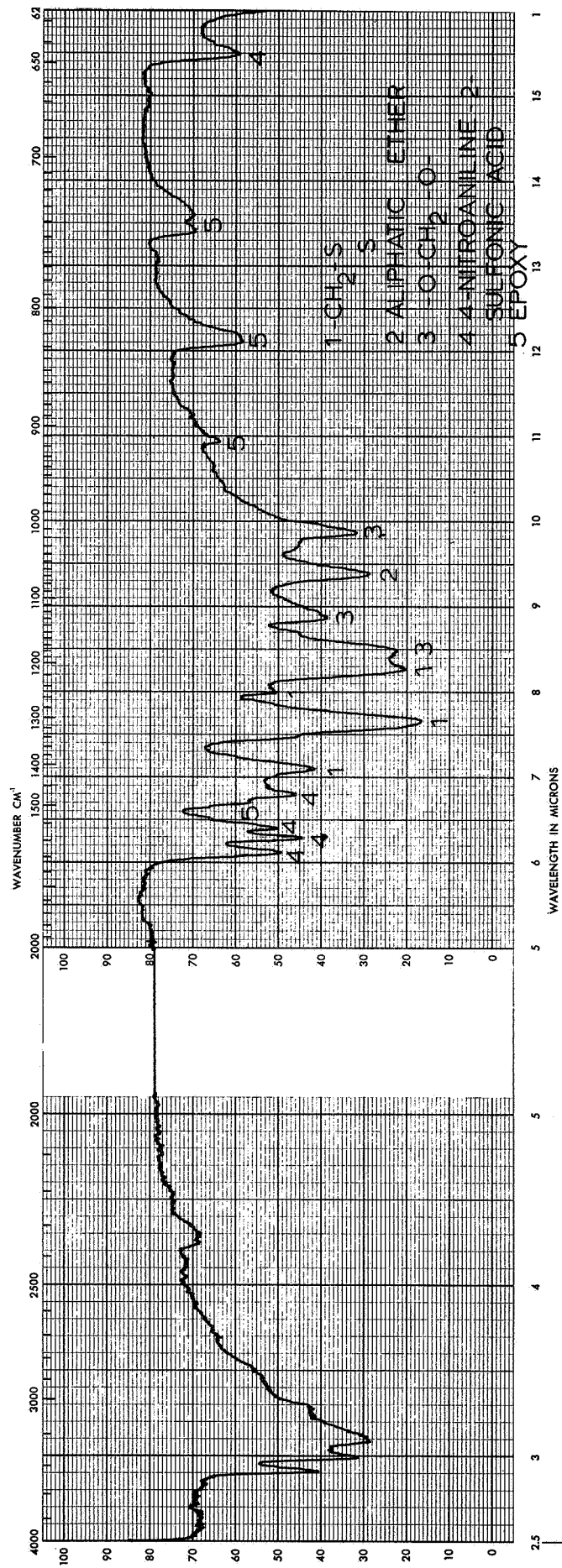


FIGURE 53. INFRARED SPECTRUM OF INTUMESCENT COATED
ISOCYANURATE FOAM (CONTROL)

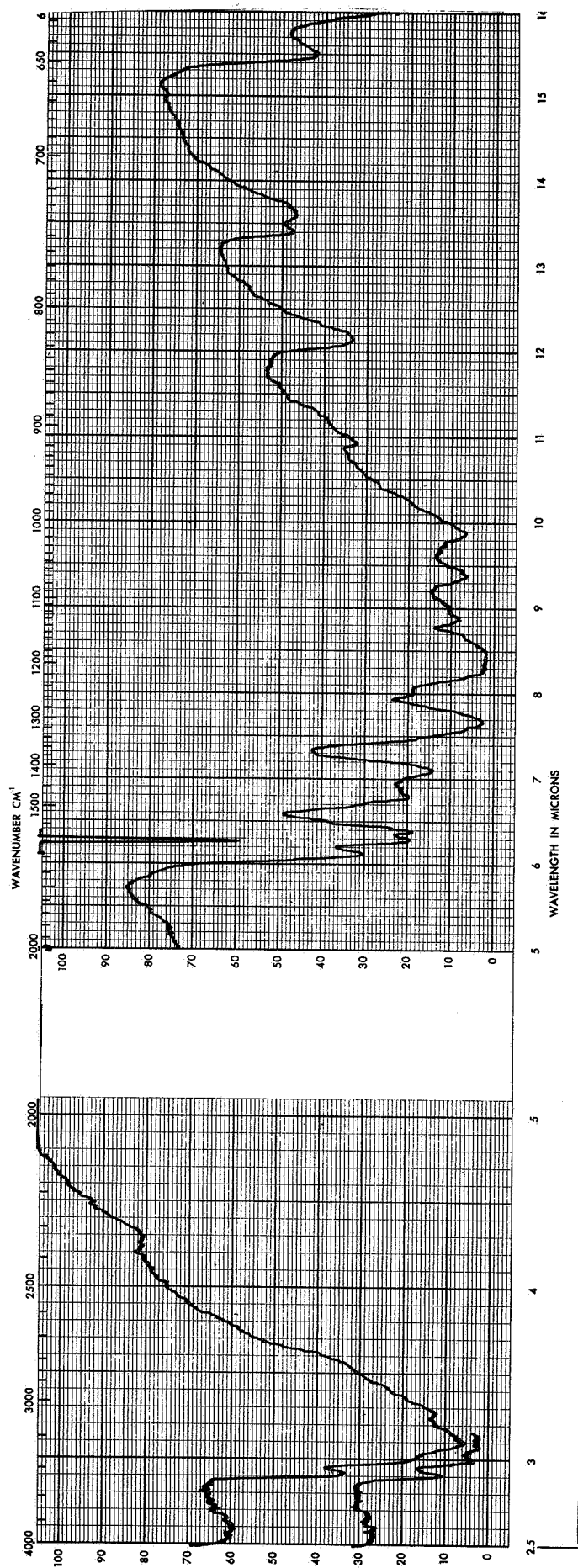


FIGURE 54. INFRARED SPECTRUM OF INTUMESCENT COATED ISOCYANURATE FOAM (100°C)

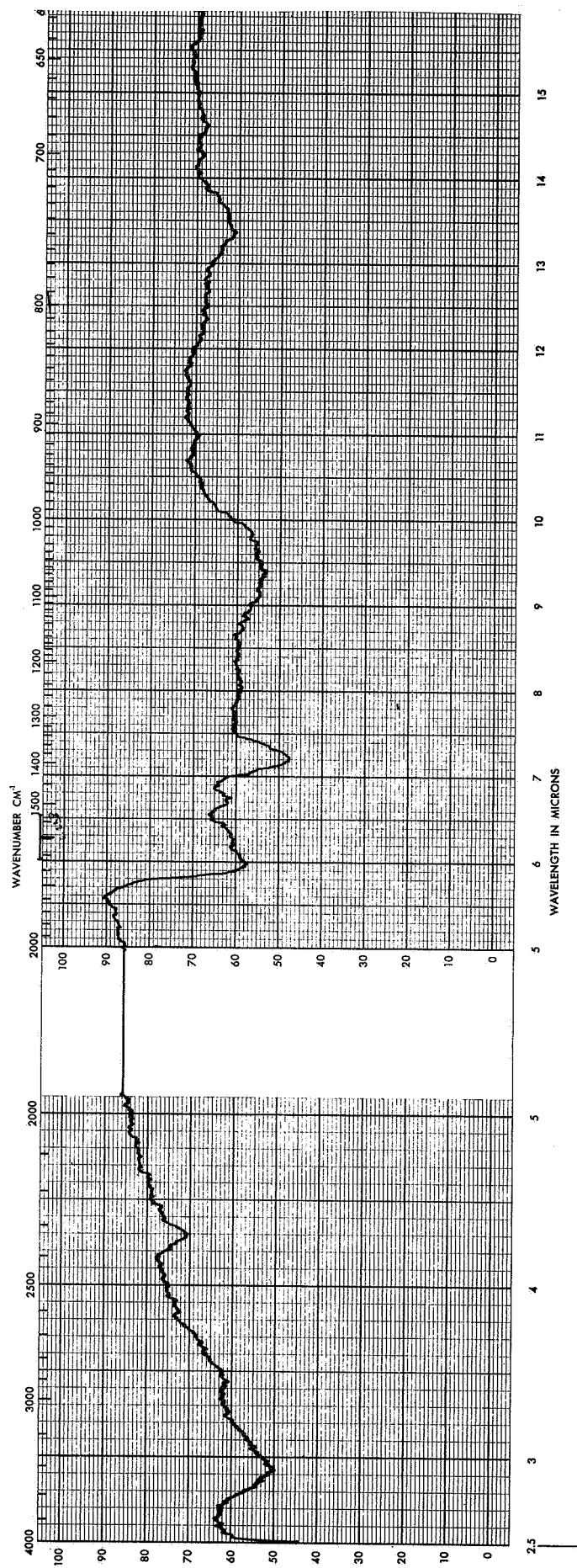


FIGURE 55. INFRARED SPECTRUM OF INTUMESCENT COATED ISOCYANURATE FOAM (200°C)

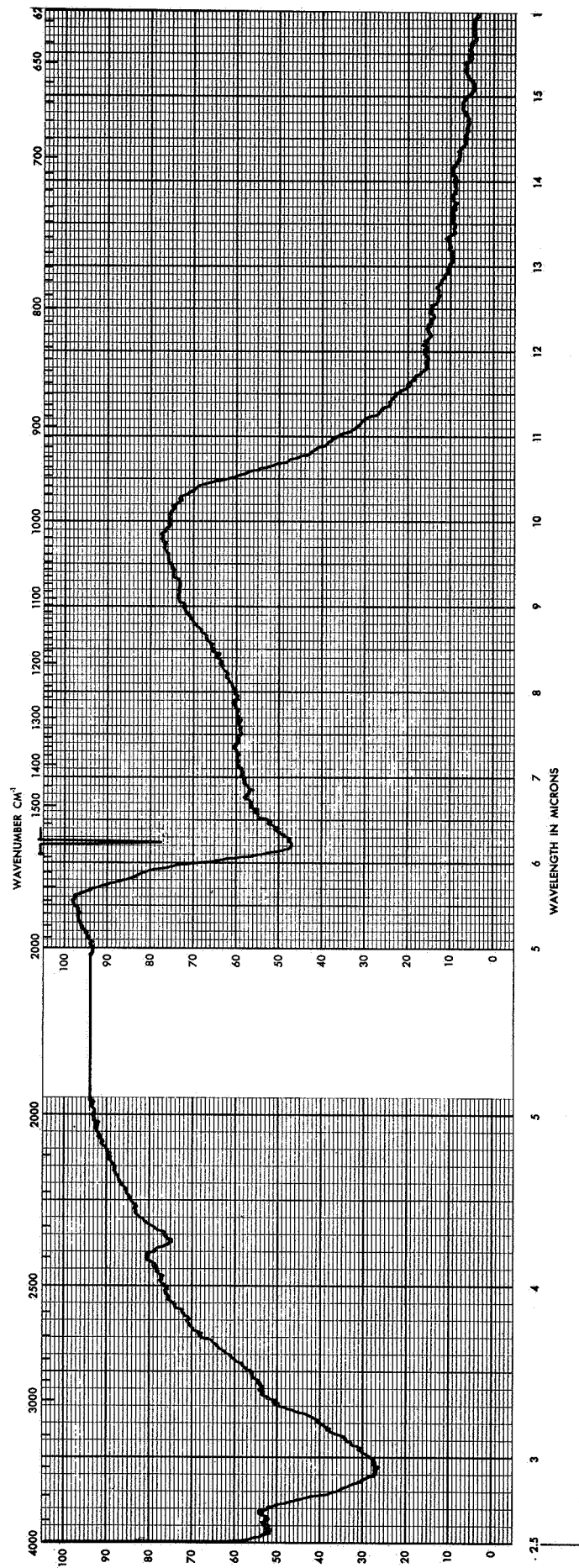


FIGURE 56. INFRARED SPECTRUM OF INTUMESCENT COATED
ISOCYANURATE FOAM (400°C)



FIGURE 57a. IGNITION



FIGURE 57b. 2 SEC.

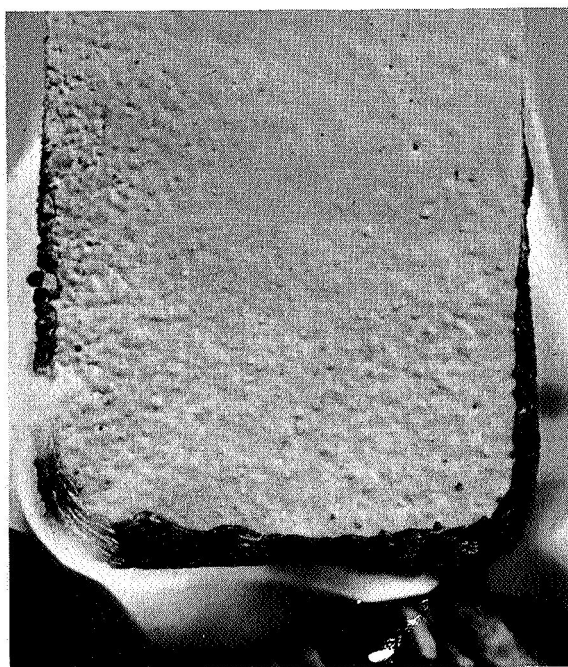


FIGURE 57c. 4 SEC.

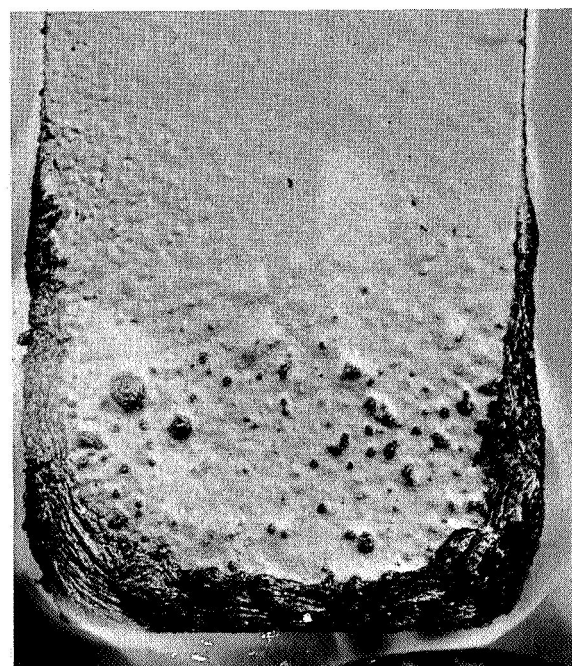


FIGURE 57d. 8 SEC.

FIGURE 57 INFRARED PHOTOGRAPHS
OF CHAR FORMATION IN
ISOCYANURATE FOAM
WITH INTUMESCENT
COATING



FIGURE 58a. 12 SEC.

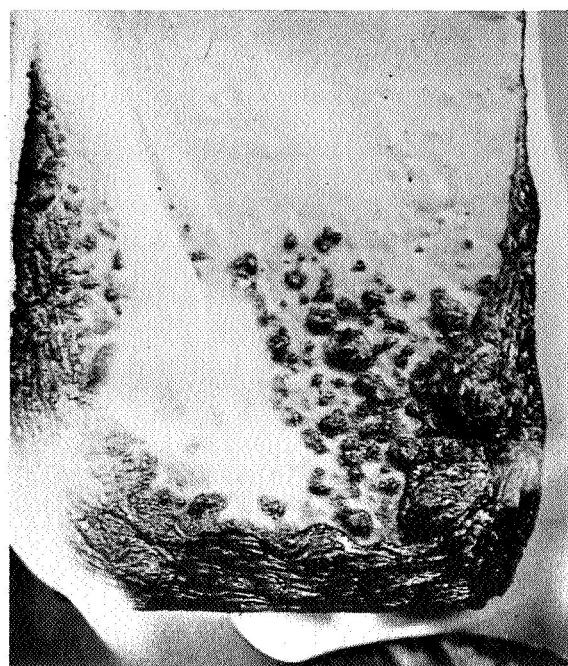


FIGURE 58b. 16 SEC.

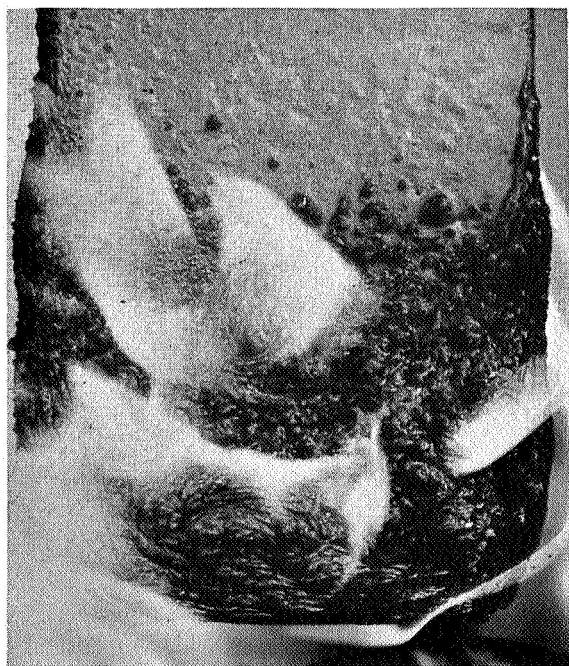


FIGURE 58c. 20 SEC.



FIGURE 58 d. 24 SEC.

FIGURE 58. INFRARED PHOTOGRAPHS OF
CHAR FORMATION IN
ISOCYANURATE FOAM WITH
INTUMESCENT COATING



FIGURE 59a. 28 SEC.



FIGURE 59b. 32 SEC.

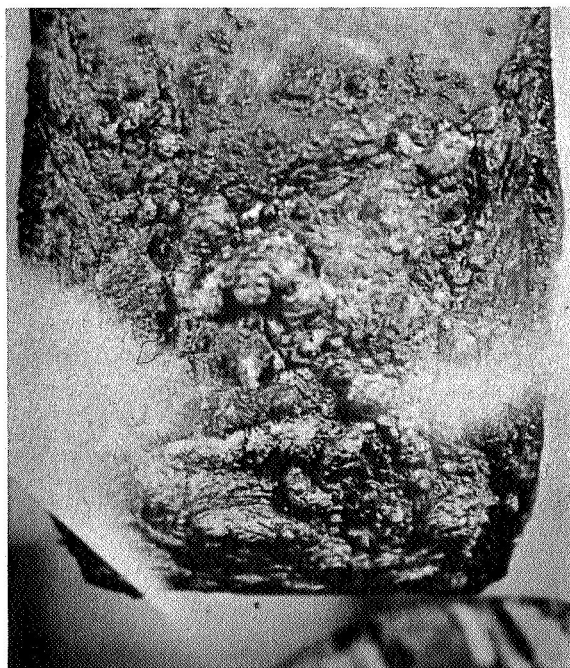


FIGURE 59c. 36 SEC.



FIGURE 59d. 40 SEC.

FIGURE 59. INFRARED PHOTOGRAPHS OF
CHAR FORMATION IN
ISOCYANURATE FOAM WITH
INTUMESCENT COATING

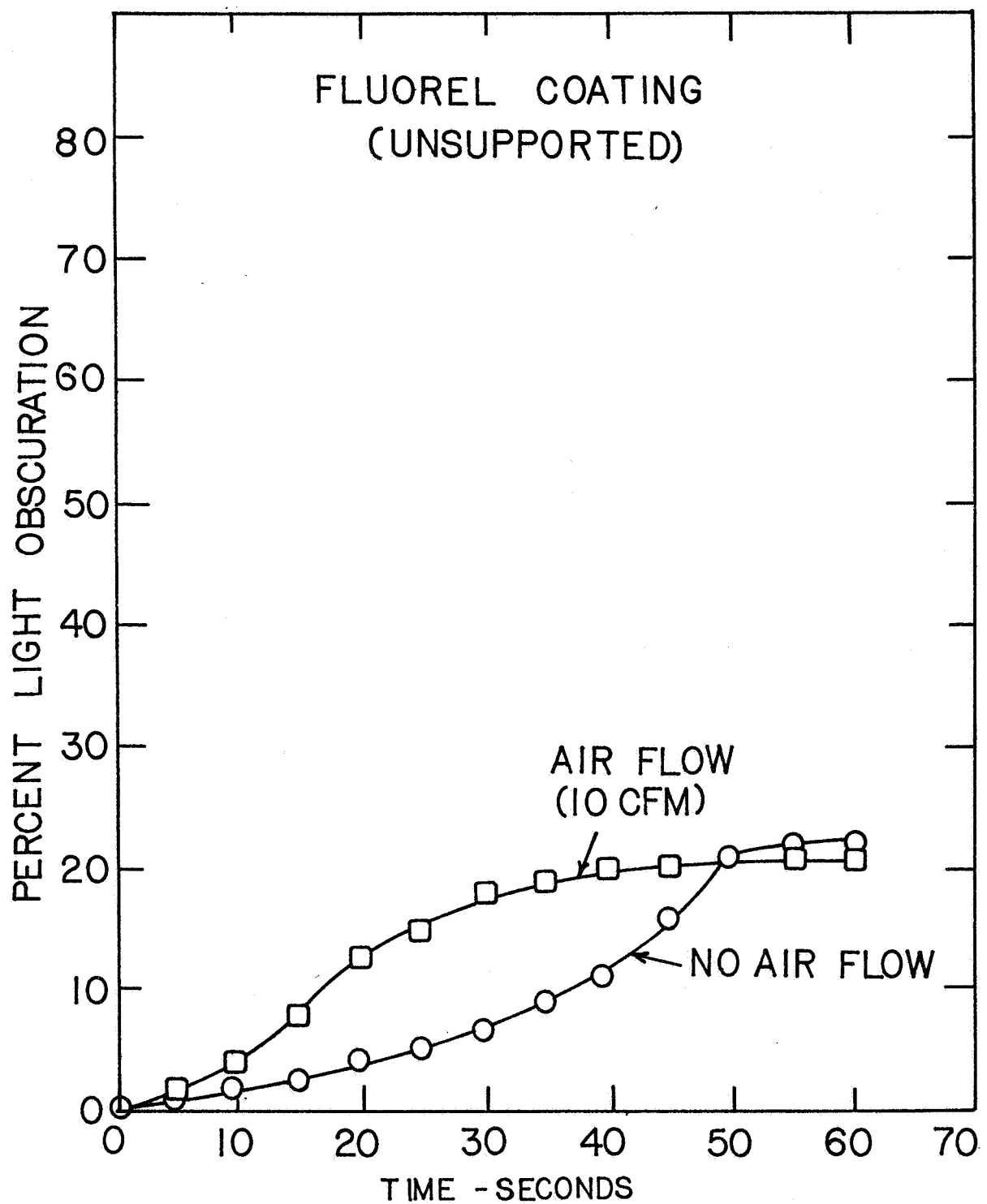


FIGURE 60. EFFECT OF COATING ON SMOKE DEVELOPMENT.

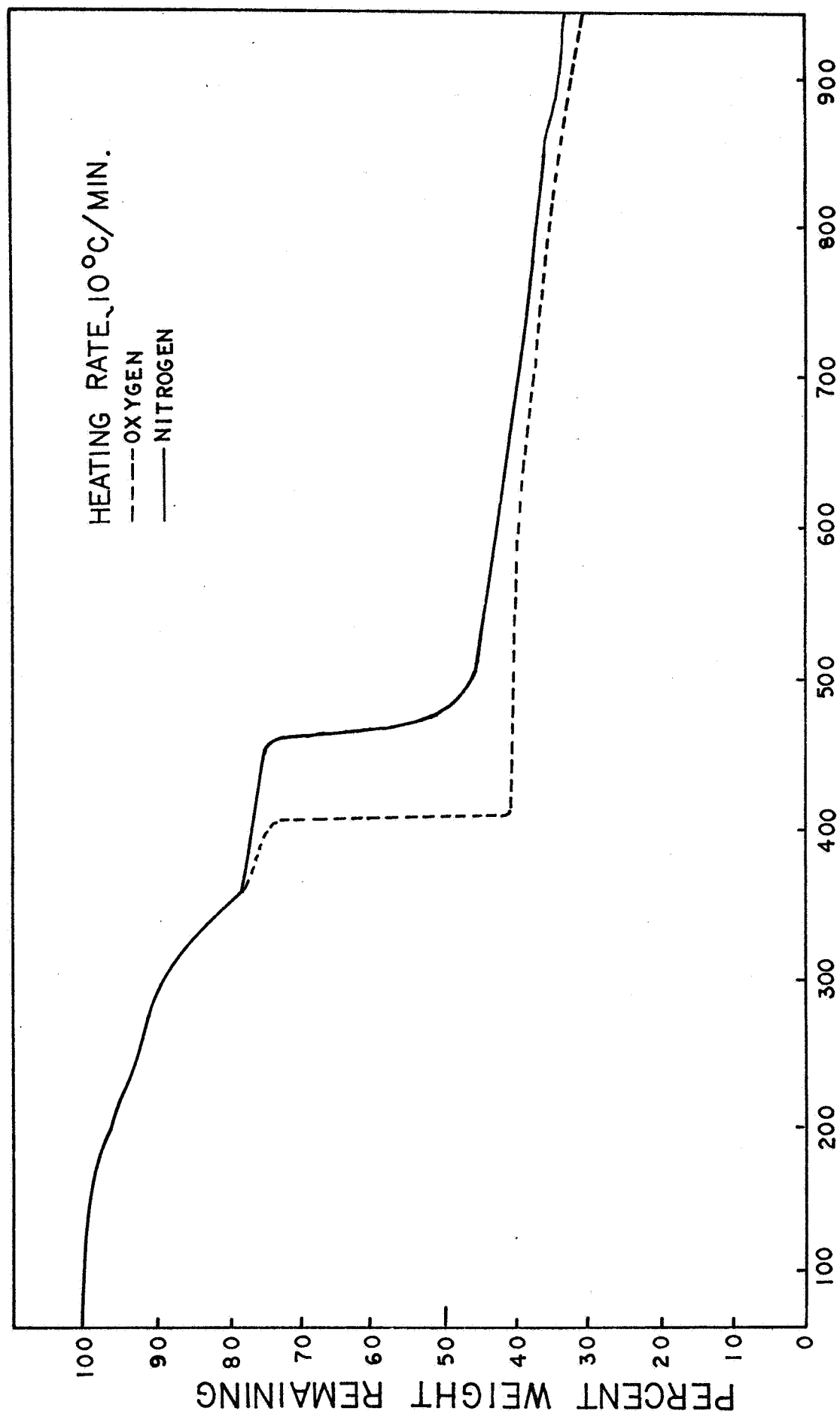


FIGURE 61. TGA OF FLUOREL REFSET.

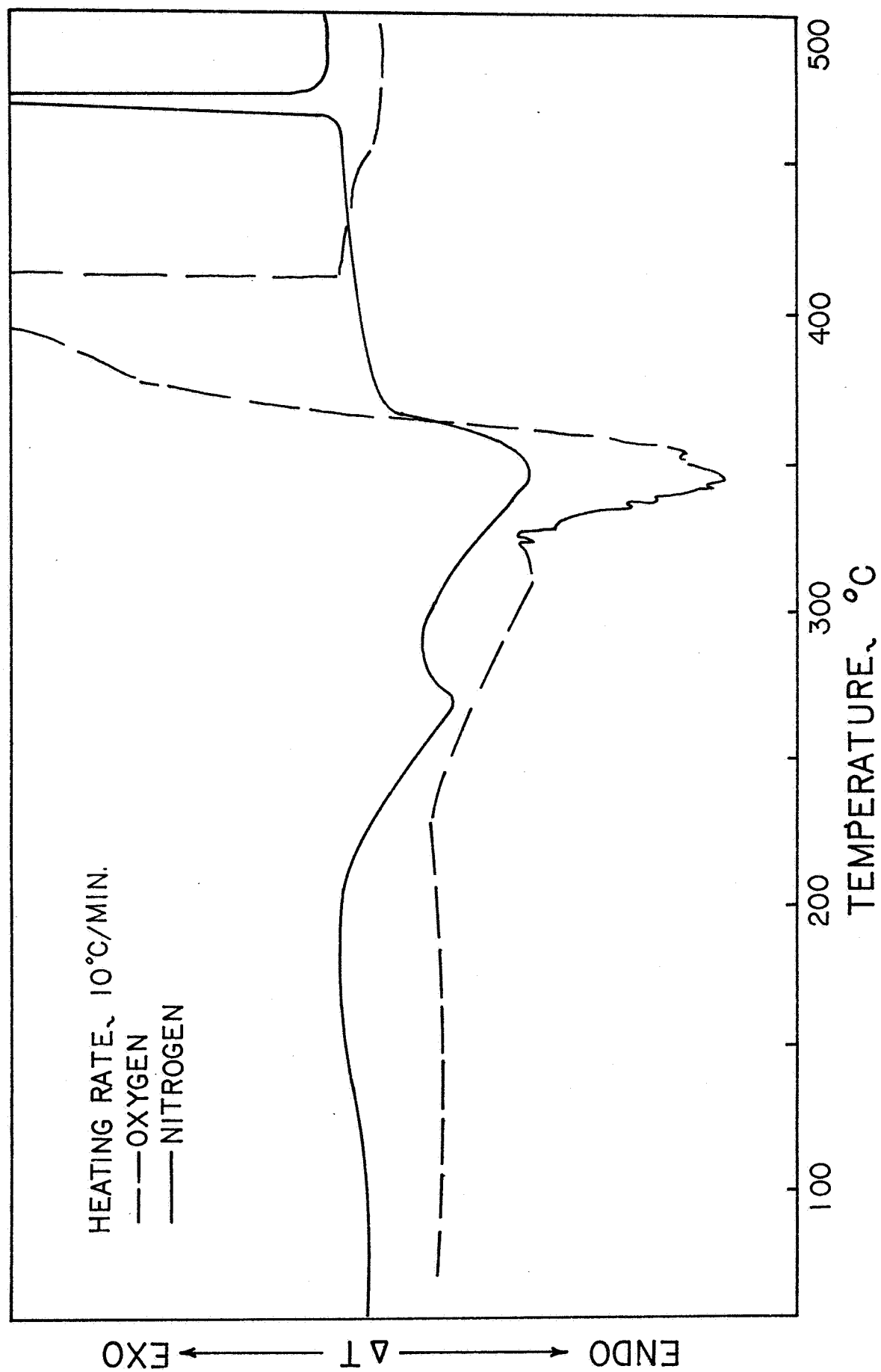


FIGURE 62. DTA OF FLUOREL REFSET.

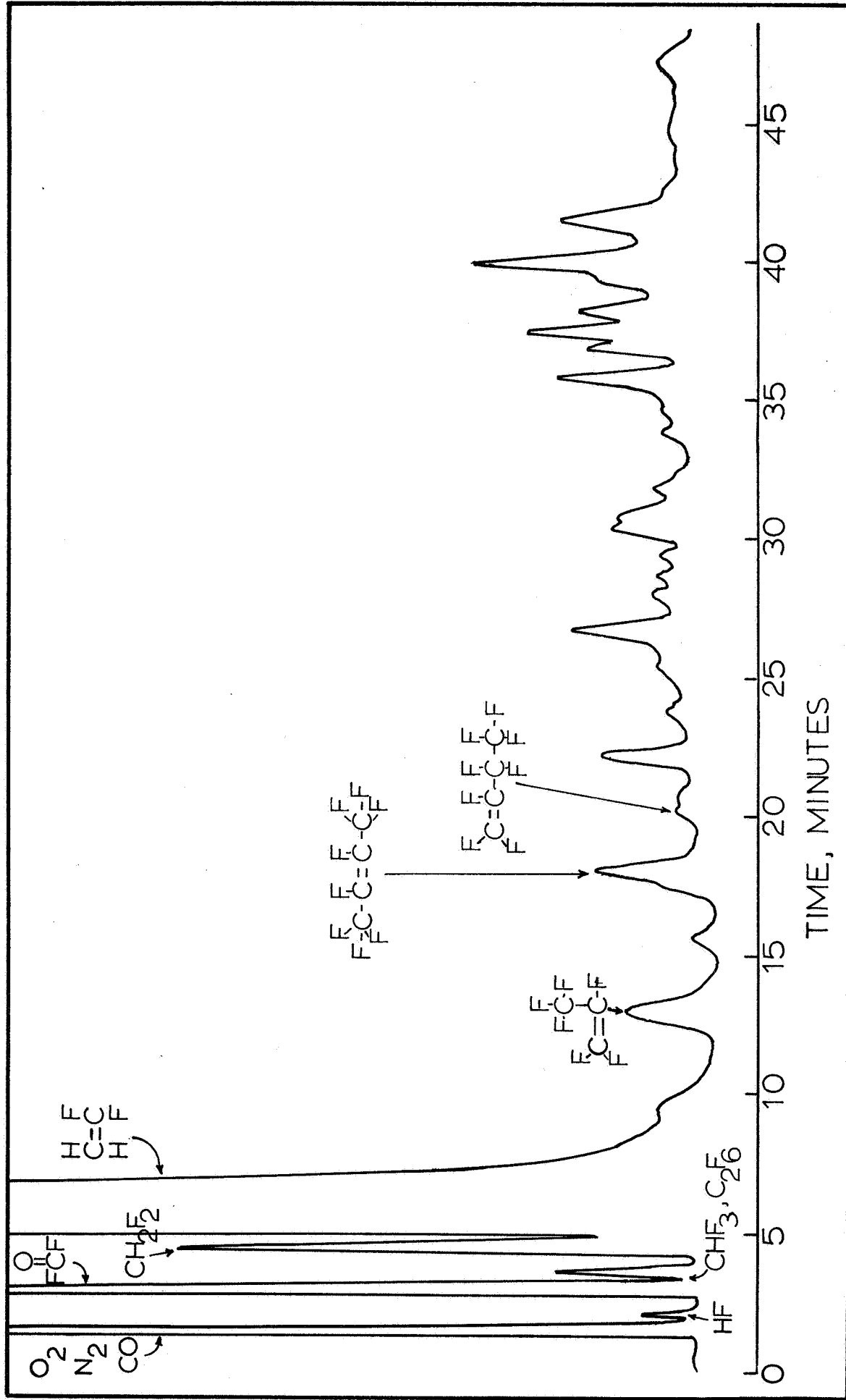


FIGURE 63. PYROLYSIS CHROMATOGRAM OF FLUOREL REFSET

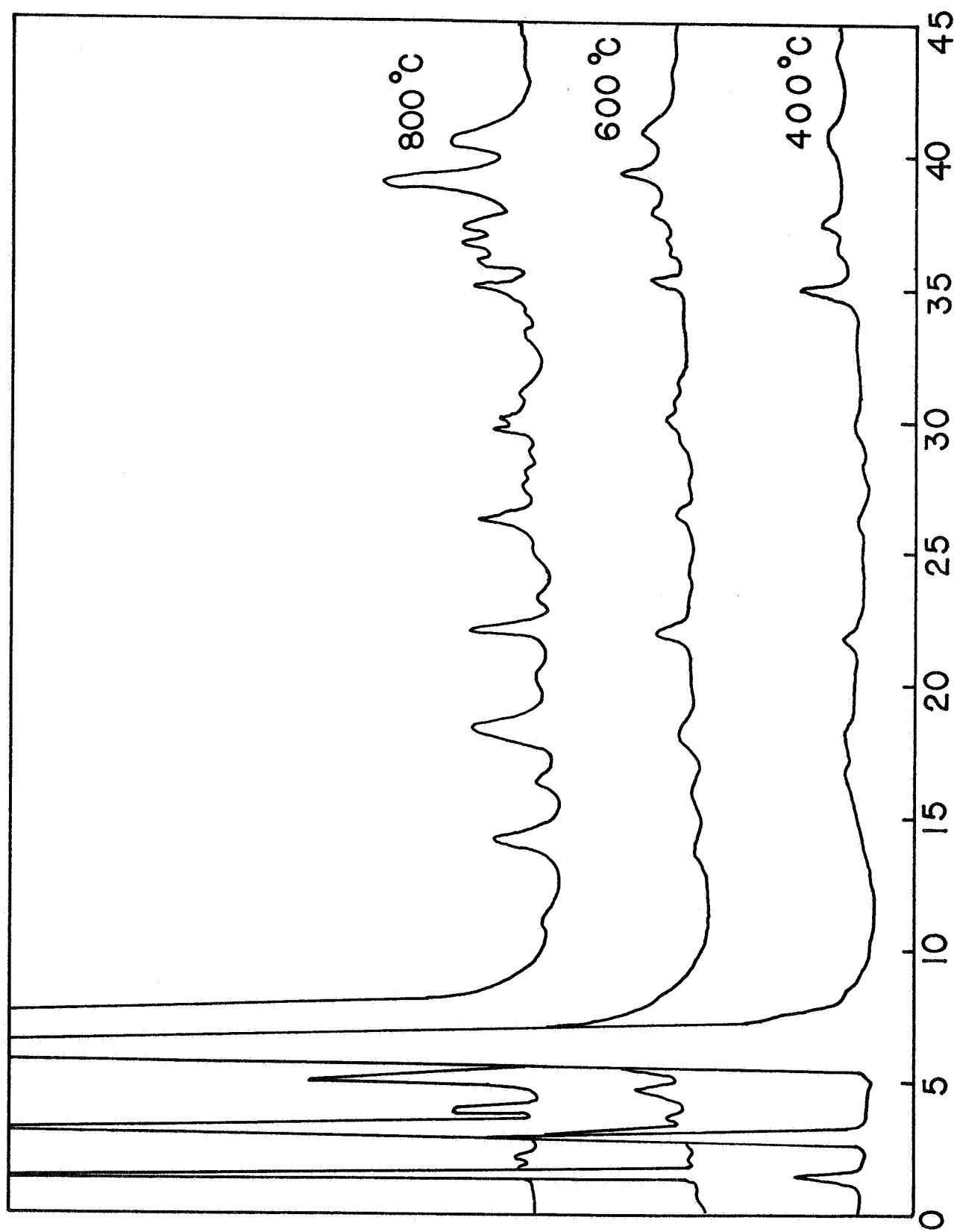


FIGURE 64. PYROLYSIS CHROMATOGRAM OF FLUOREL REFSET.

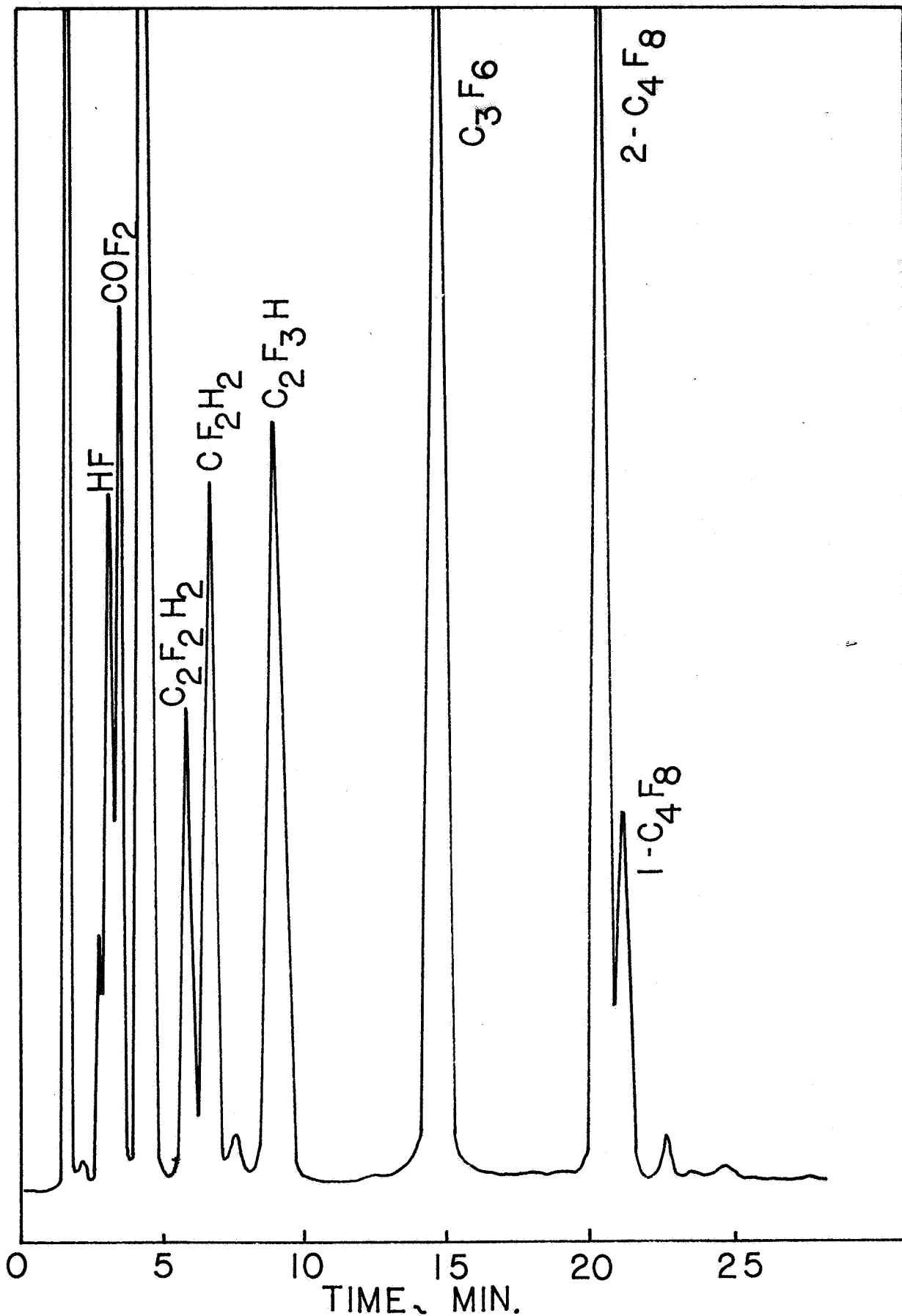


FIGURE 65. CHROMATOGRAM OF SELECTED FLUORINATED GASES.

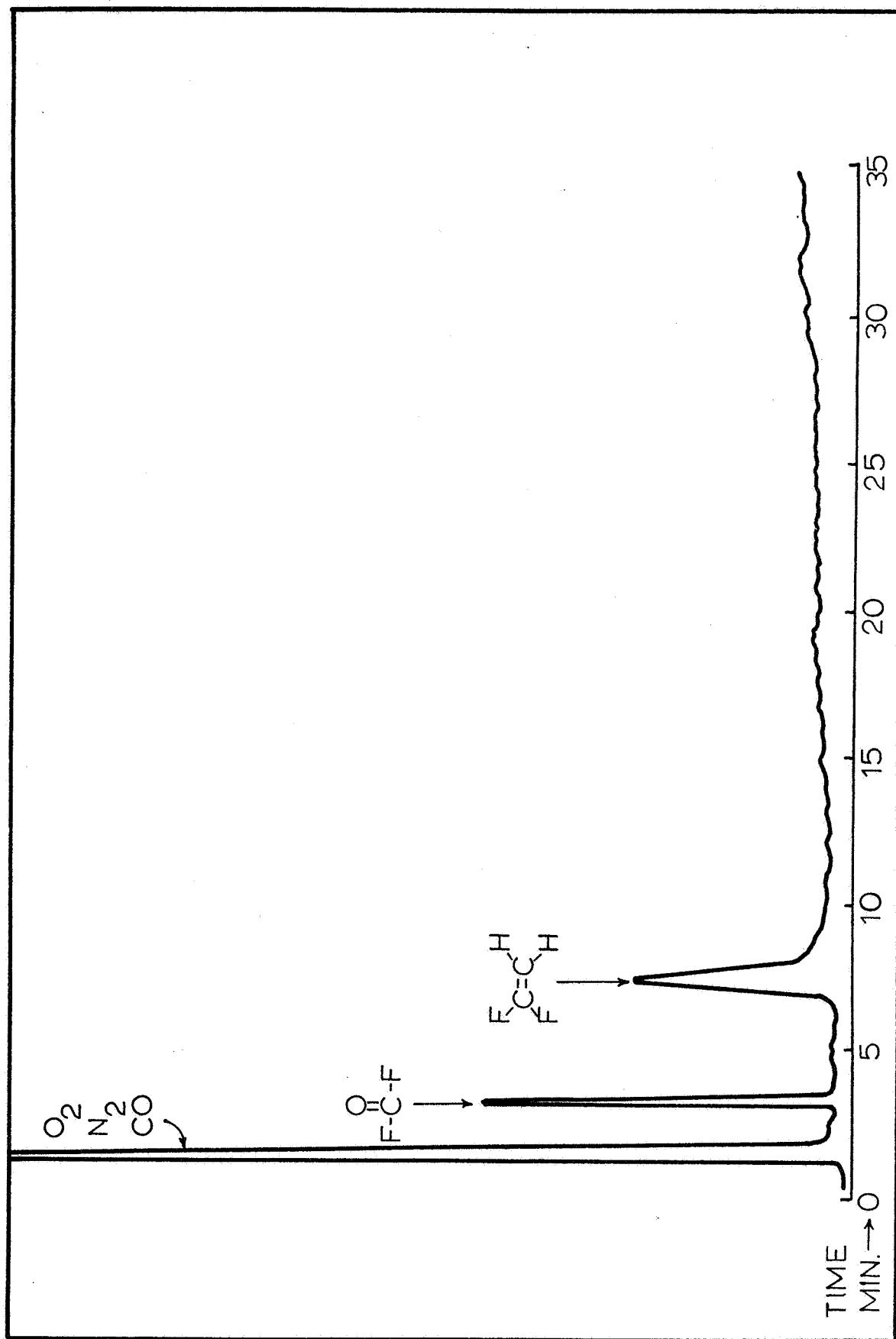


FIGURE 66. CHROMATOGRAM OF OXIDATIVE DEGRADATION PRODUCTS OF
FLUOREL REFSET

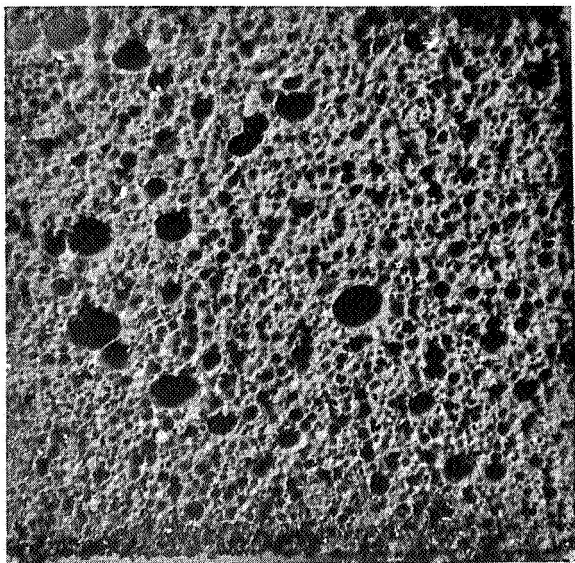


FIGURE 67a. CONTROL

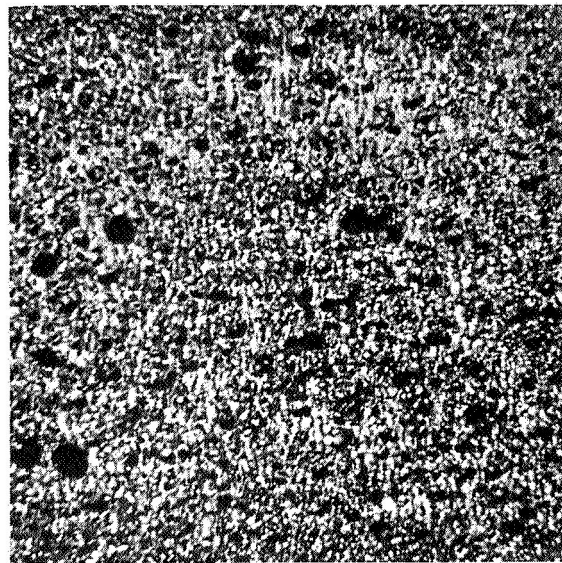


FIGURE 67b. 100°C.

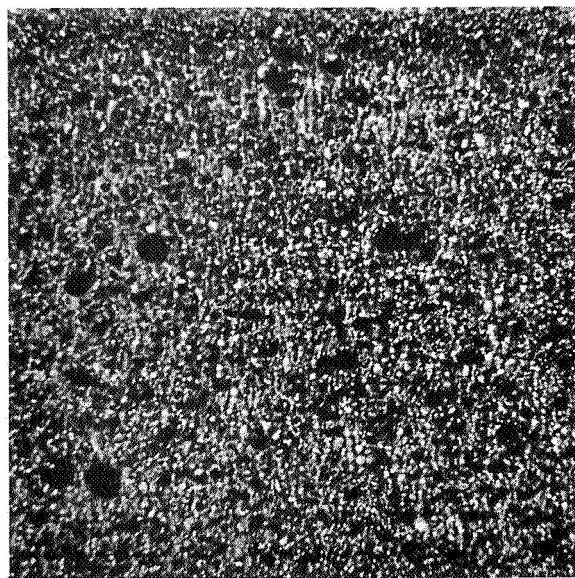


FIGURE 67c. 200°C.

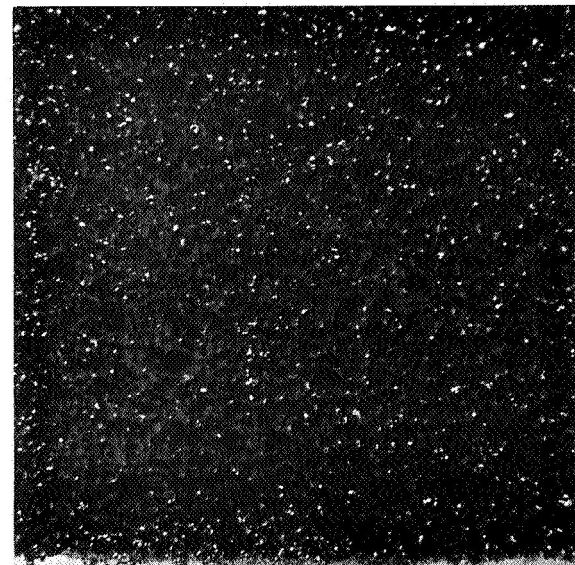


FIGURE 67d. 300°C.

FIGURE 67 OXIDATIVE DEGRADATION OF FLUOREL COATED FOAM

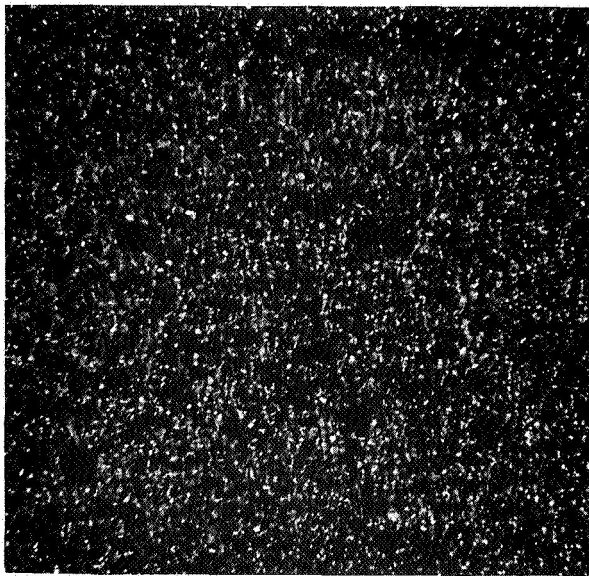


FIGURE 68a. 400°C.

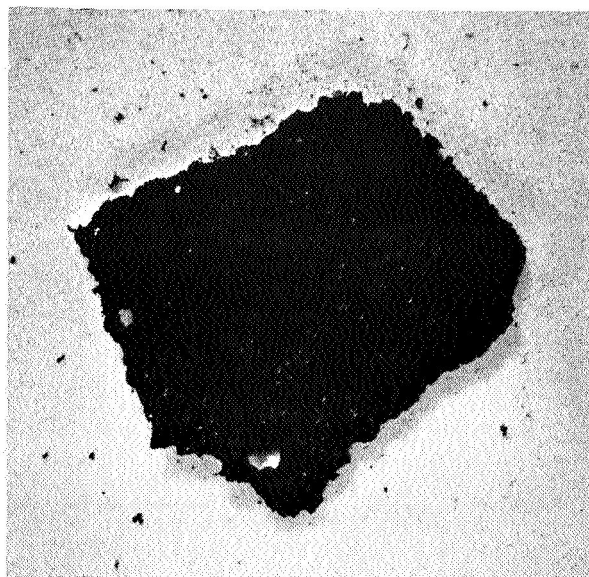


FIGURE 68b.

FIGURE 68. OXIDATIVE DEGRADATION OF
FLUOREL COATED FOAM

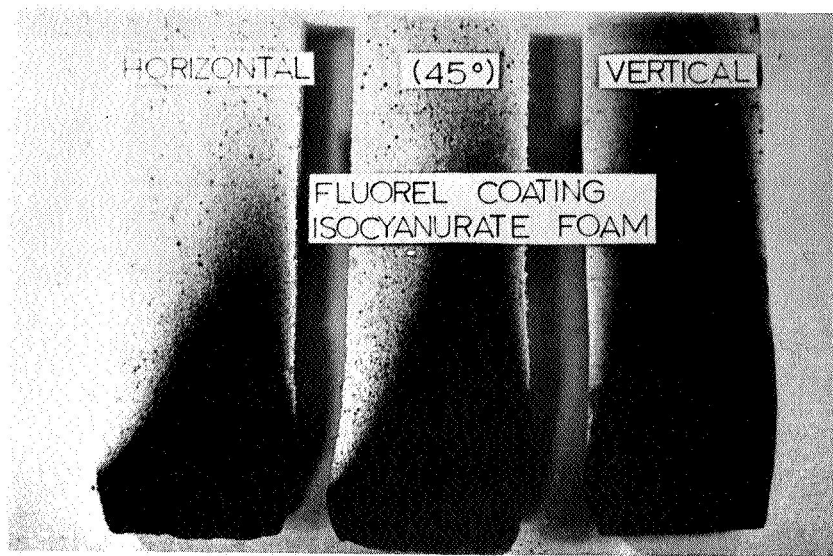


FIGURE 69. ASTM D-1692
(TOP VIEW)

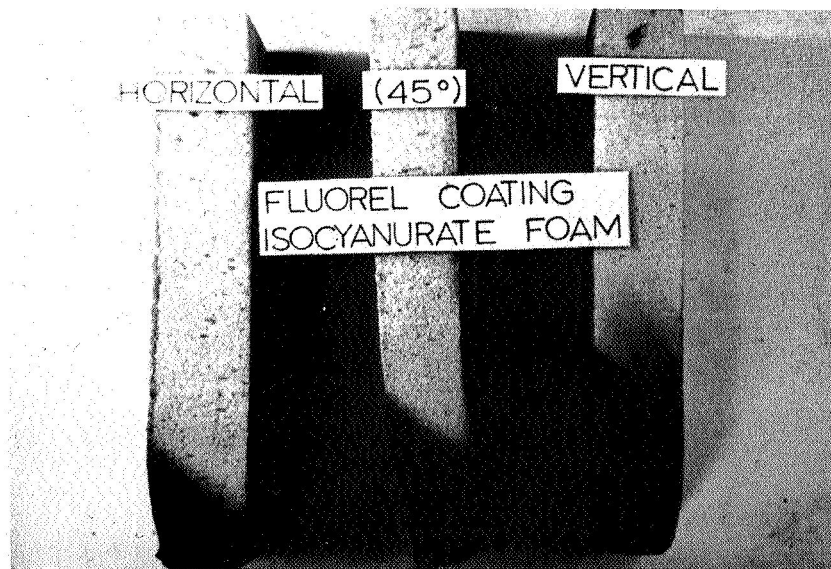


FIGURE 69. ASTM D-1692
(EDGE VIEW)

FIGURE 69. COMPOSITE - BURNED
SAMPLES ASTM D-1692 TEST

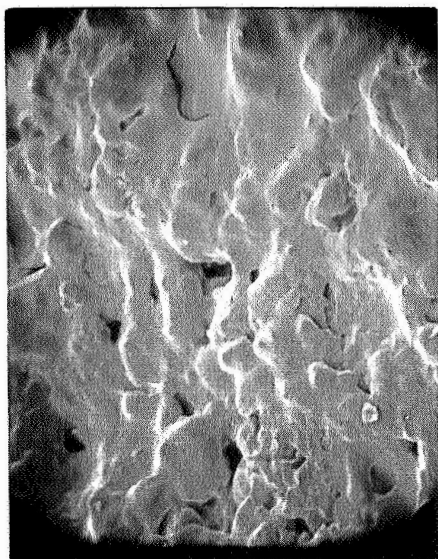


FIGURE 70a. CONTROL- 550X

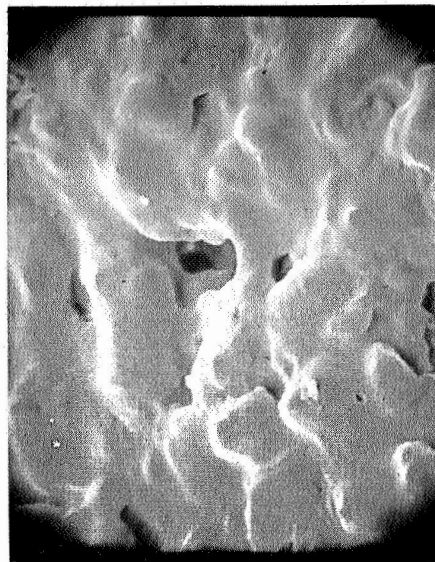


FIGURE 70b. CONTROL-1100X

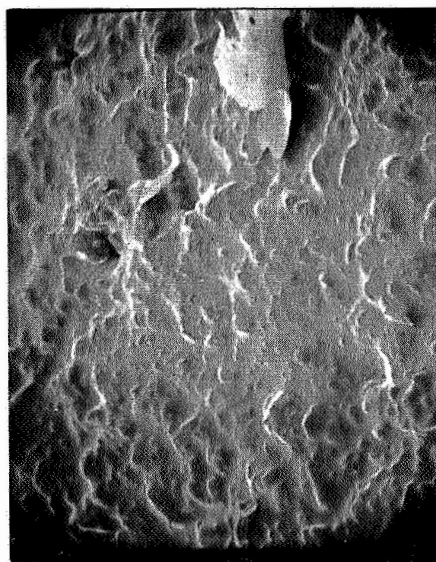


FIGURE 70c. 100°C - 220X

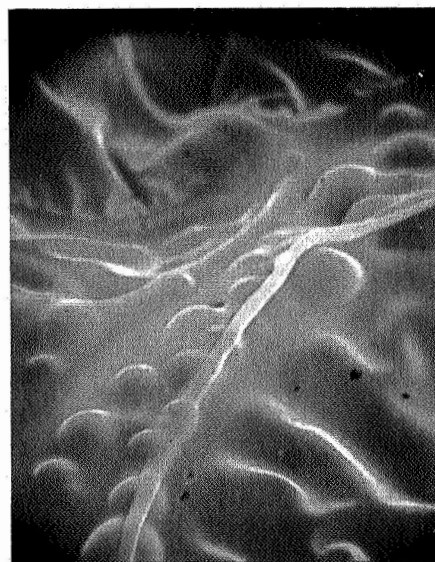


FIGURE 70d. 300°C - 2600X

FIGURE 70. OXIDATIVE DEGRADATION OF
FLUOREL COATED ISOCYANURATE FOAM

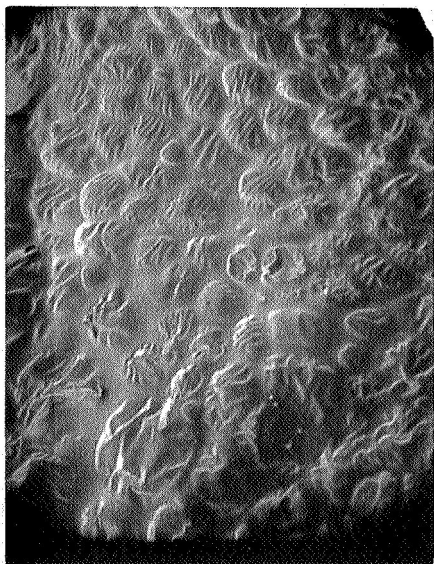


FIGURE 71a. 200°C - 110X



FIGURE 71b. 200°C - 225X



FIGURE 71c. 300°C - 260X

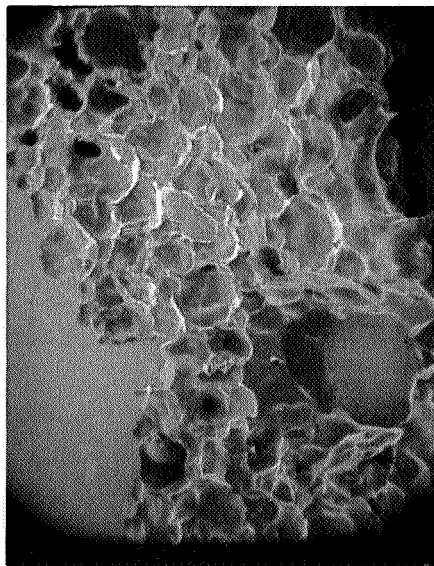


FIGURE 71d. 500°C - 20X

FIGURE 71. OXIDATIVE DEGRADATION OF
FLUOREL COATED ISOCYANURATE FOAM

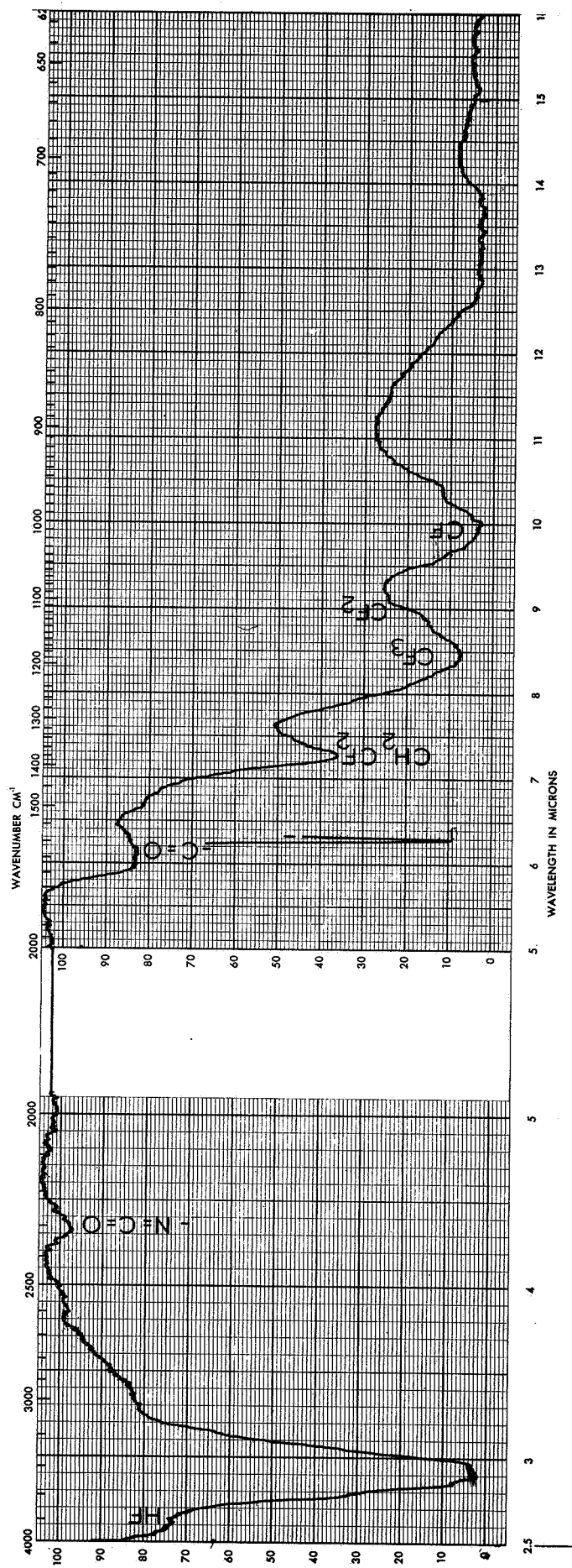


FIGURE 72. INFRARED SPECTRUM OF FLUOREL COATED ISOCYANURATE FOAM (CONTROL)

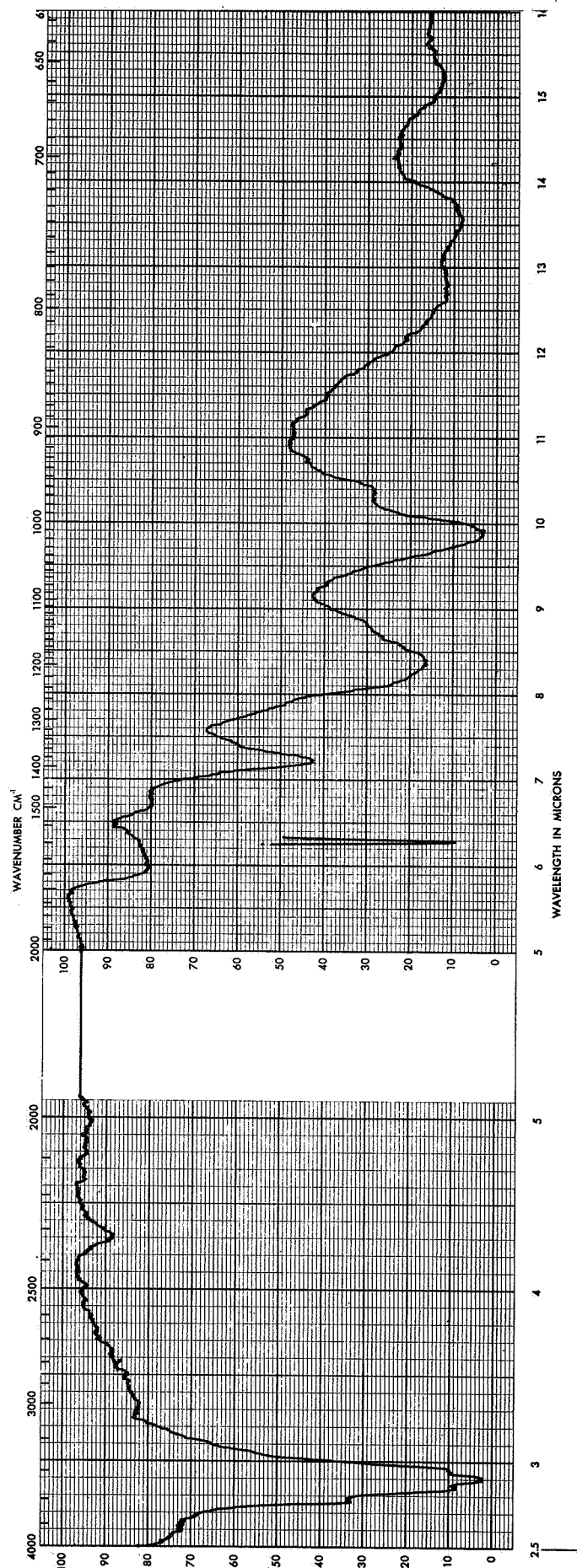


FIGURE 73. INFRARED SPECTRUM OF FLUOREL COATED
ISOCYANURATE FOAM (100°C)

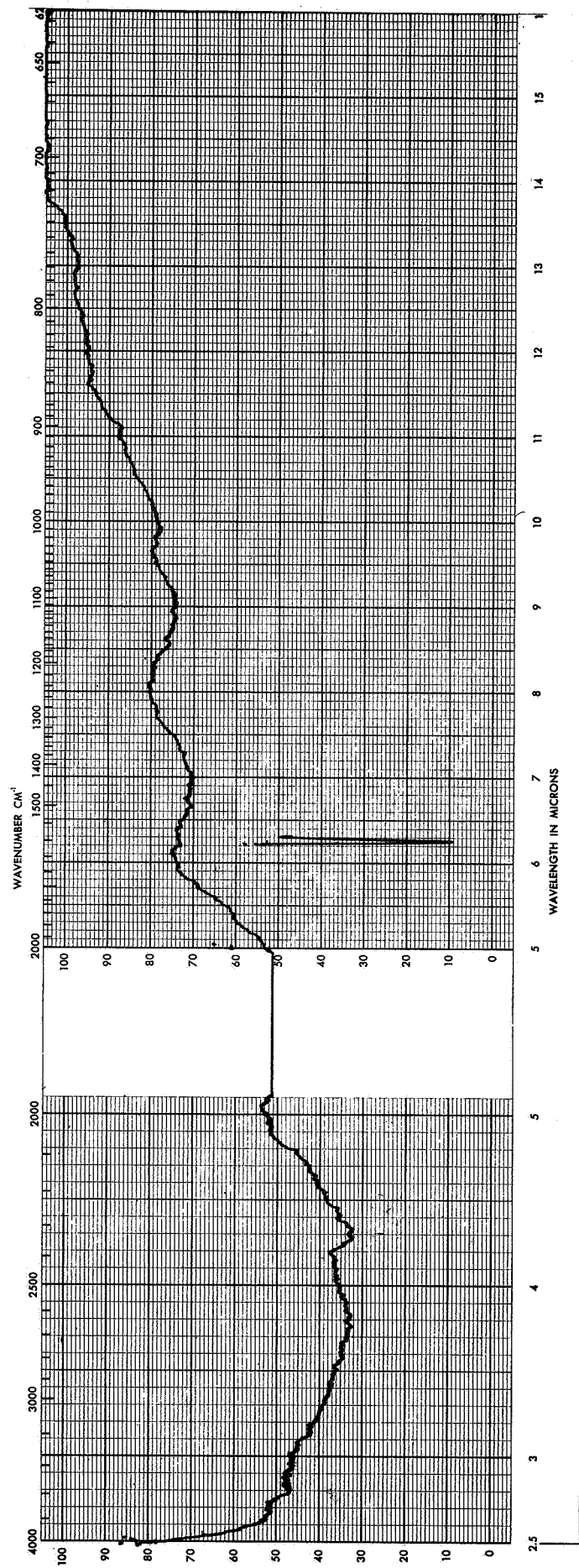


FIGURE 74. INFRARED SPECTRUM OF FLUOREL COATED ISOCYANURATE FOAM (200°C)

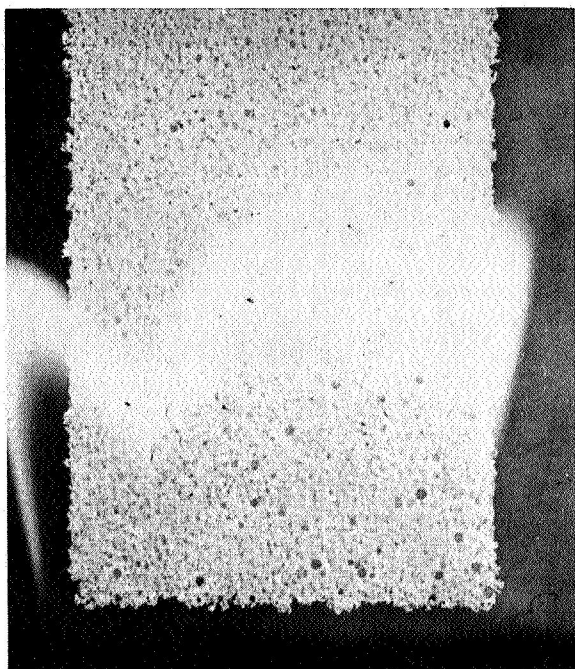


FIGURE 75a. IGNITION

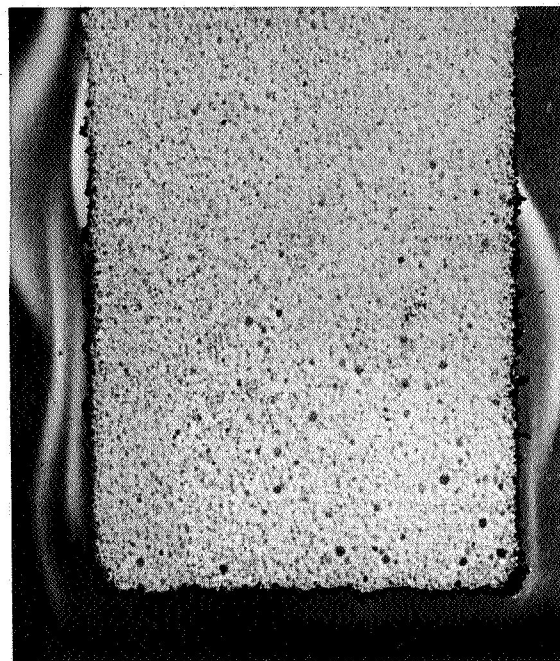


FIGURE 75b. 2 SEC.

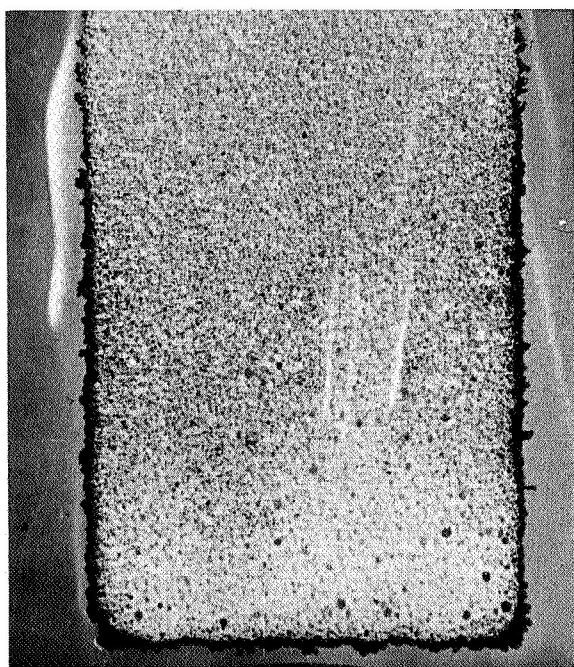


FIGURE 75c. 4 SEC.

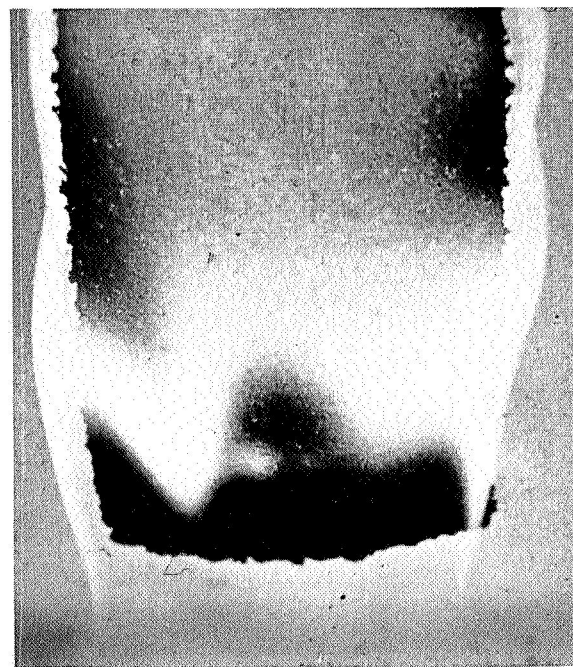


FIGURE 75d. 8 SEC.

FIGURE 75. INFRARED PHOTOGRAPHS OF
CHAR FORMATION IN
FLUOREL COATED FOAM

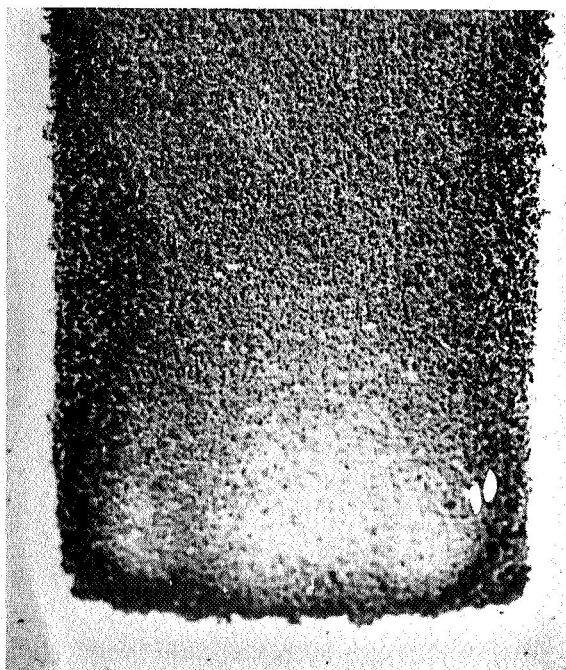


FIGURE 76a. 12 SEC.

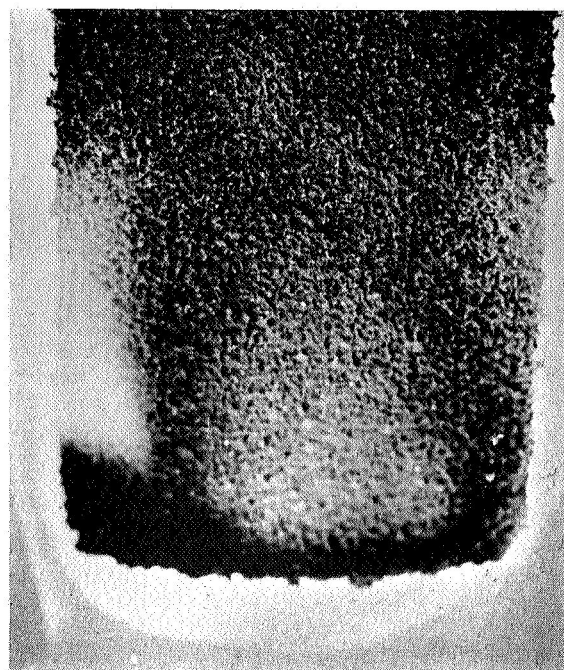


FIGURE 76b. 16 SEC.

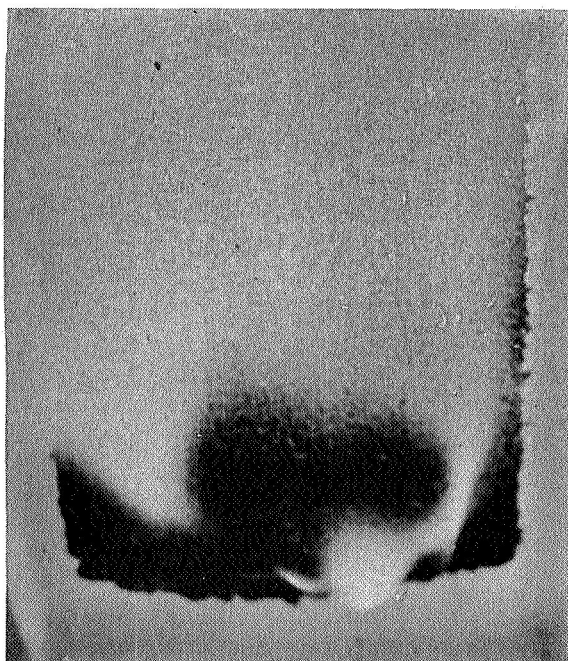


FIGURE 76c. 20 SEC.

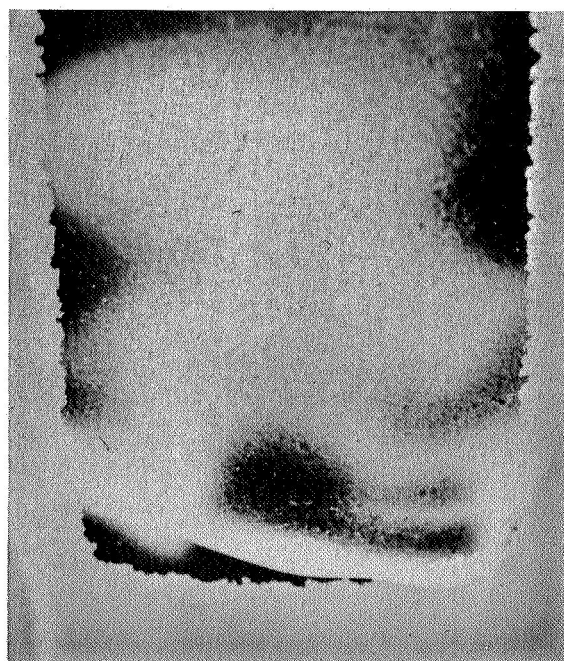


FIGURE 76d. 24 SEC.

FIGURE 76. INFRARED PHOTOGRAPHS OF
CHAR FORMATION IN
FLUOREL COATED FOAM

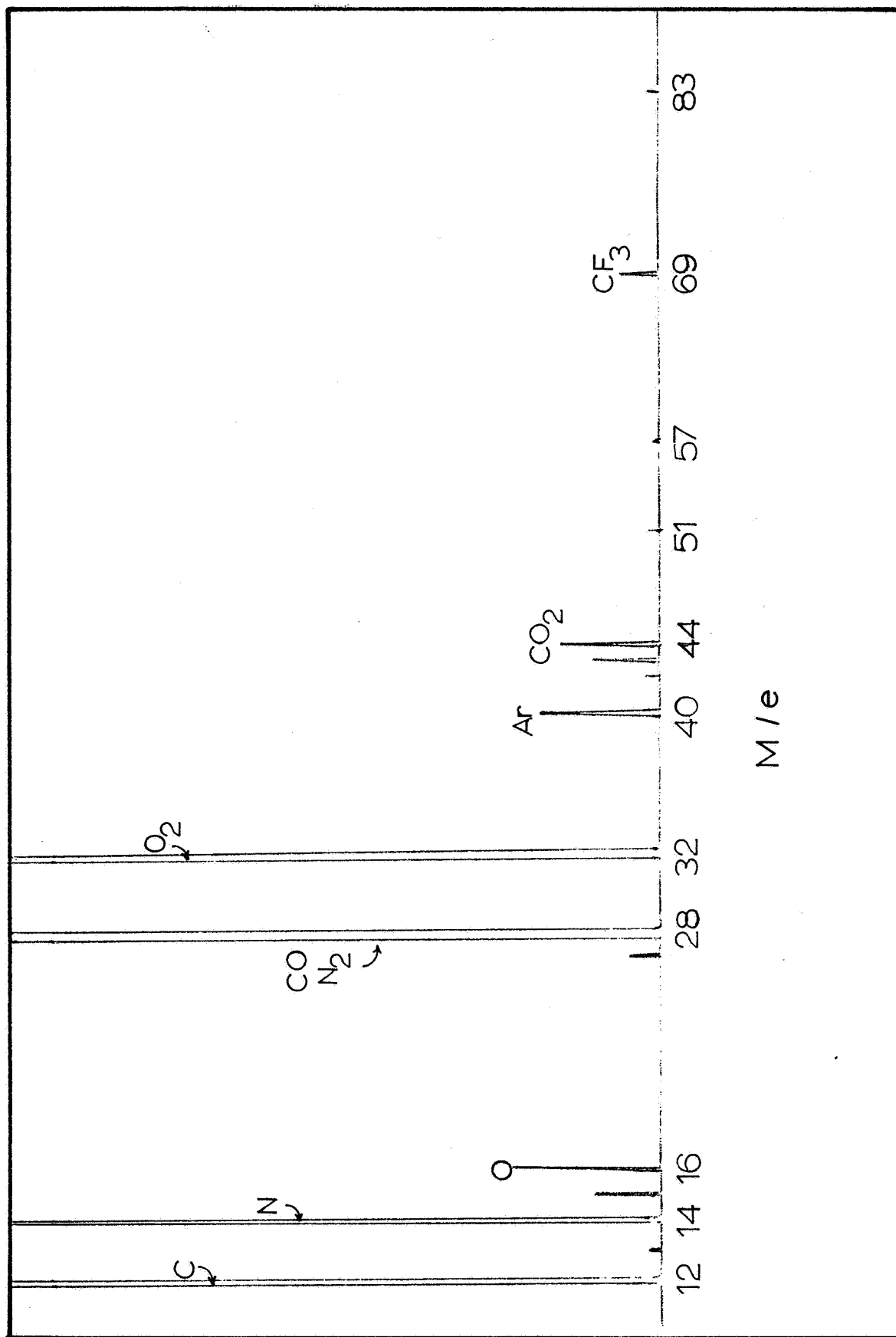


FIGURE 77. MASS SPECTRUM OF EXPERIMENTAL ATMOSPHERE

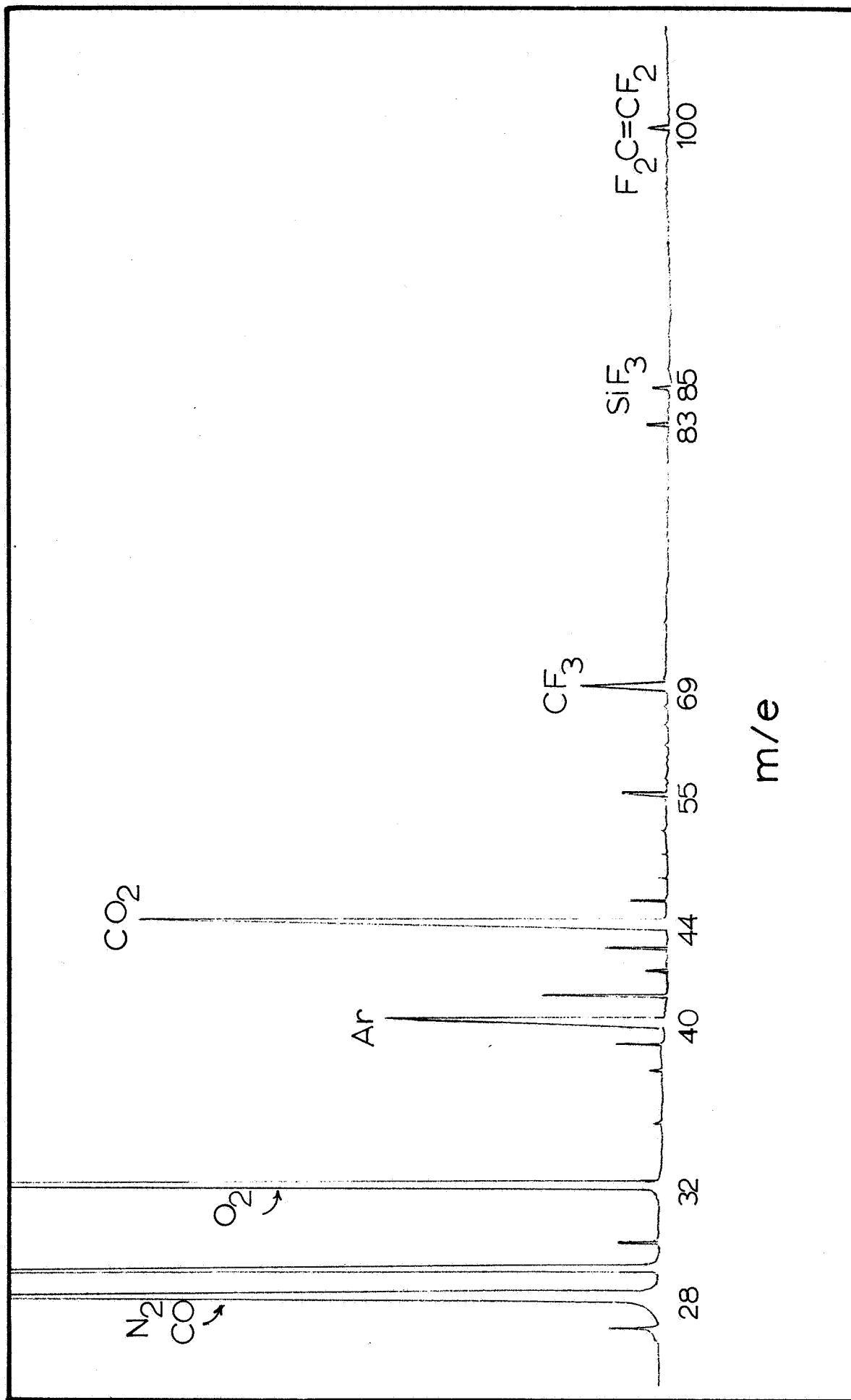


FIGURE 78. MASS SPECTRUM OF EXPERIMENTAL ATMOSPHERE